

CO₂-DRIVEN OSCILLATIONS IN METHANE MILD COMBUSTION

A. Chinnici***, M. de Joannon**, P. Sabia**,
A. Picarelli*, R. Ragucci**

alfonso.chinnici@unina.it

* Dipartimento di Ingegneria Chimica, P.le Tecchio, 80, 80125, Naples, Italy

** Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio, 80, 80125, Naples, Italy

Abstract

The aim of the work is to numerically study the oxidation process of methane in typical condition of MILD combustion in systems highly diluted in CO₂. Simulations have been performed in a perfect stirred flow reactor at atmospheric pressure. The analyses have been realized as function of the main parameters of the system, namely mixture inlet temperatures, mixture compositions and reactor heat loss coefficient values.

Previous experimental and numerical works carried out in a non-adiabatic perfect stirred flow reactor showed a complex dynamic behavior of methane/oxygen systems highly diluted in nitrogen or steam. More specifically, thermo-kinetics temperature oscillations were observed.

The main result obtained with respect to previous works is that the presence of carbon dioxide in the combustion system leads to the establishment of temperature oscillations even for adiabatic conditions, so that temperature oscillations are kinetic-driven.

In fuel lean conditions the CO/CO₂ equilibrium inter-conversion plays a key role in the establishment of dynamic behavior; in rich fuel conditions the CH₃ recombination path, active at relatively high working temperatures, modulates temperature oscillations.

In agreement with previous works, in case of non-adiabatic systems, temperature oscillations are influenced by the heat loss towards the surrounding.

Introduction

Demand on reducing pollutants emissions, in relation to the increasingly stringent environmental rules, has led to investigate new combustion technologies that could match with these requirements. In this framework, MILD combustion [1] appears as one of the most promising innovative technologies for producing energy in a clean and efficient way. It is characterized by elevated reactants temperatures and mixture highly diluted. These conditions lead to a “volume combustion” featuring a controlled volumetric reaction rate and moderate local over-temperatures and gradients. Typical working temperatures are not crucial for thermal NO_x and soot production. The dilution and the pre-heating of fresh reactant mixtures are

realized through a recycling of exhausted gases and thus, fuel oxidation process occurs in presence of great amount of CO_2 and water.

Under such operative conditions, the kinetic evolution of the oxidation process is very different from traditional combustion systems. In particular the high inlet temperature and high mixture dilution level can significantly affect the evolution of hydrocarbons combustion process. Furthermore, CO_2 and steam can modify the chemical pathways involved in oxidation processes because of thermal and kinetic effects [2, 3].

Previous experimental and numerical works [4, 5, 6, 7] carried out in an atmospheric non-adiabatic perfect stirred flow reactor showed a complex dynamic behavior of methane/oxygen systems highly diluted in nitrogen or steam. Thermo-kinetic temperature oscillations were identified. Their amplitude and frequencies strongly depend on the mixture inlet temperature and composition. This dynamic behavior was explained on the basis of chemical competition between different kinetic pathways. The CH_3 recombination path present in the methane oxidation mechanism plays a key role in modulation of temperature oscillations.

The aim of the present work is to numerically study oxidation process of methane in typical condition of MILD combustion in systems highly diluted in CO_2 in order to evaluate the effect of carbon dioxide dilution on the evolution of the combustion process.

Simulations have been performed in a perfect stirred flow reactor. The analyses have been realized as function of the main parameters of the system, namely mixture inlet temperatures, mixture compositions and reactor heat loss coefficient values.

Numerical Tools

In this work, the transient Perfectly Stirred Reactor (PSR) model of the Chemkin package [8] and the detailed kinetic mechanism c1-c3 [9] were used. The modeled reactor has a volume of 100 cm^3 and an internal surface area of 104 cm^2 , following indications from previous works [4, 5, 6, 7].

Numerical simulations were carried out at atmospheric pressure for different inlet temperatures (T_{in}) and mixtures compositions. In particular, the carbon/oxygen (C/O) feed ratio was changed from values close to zero up to 0.5. For each C/O ratio, inlet temperature was varied from 1000 K up to 1500 K.

Adiabatic and non-adiabatic conditions were investigated. For non-adiabatic case the heat transfer coefficient is $0.02 \text{ cal/cm}^2 \text{ K s}$. Reactor residence time and CO_2 mixture dilution level were set equal to 0.5 s and 90% respectively.

Results and discussions

Numerical simulations carried out changing the mixture inlet temperatures and compositions evidenced the presence of several combustion regimes in both adiabatic and non-adiabatic conditions. On the basis of temporal temperature profiles they were resumed in the T_{in} -C/O plane (Figure 1). In particular, non-

reactive, steady combustion, dynamic and damped oscillations areas were identified.

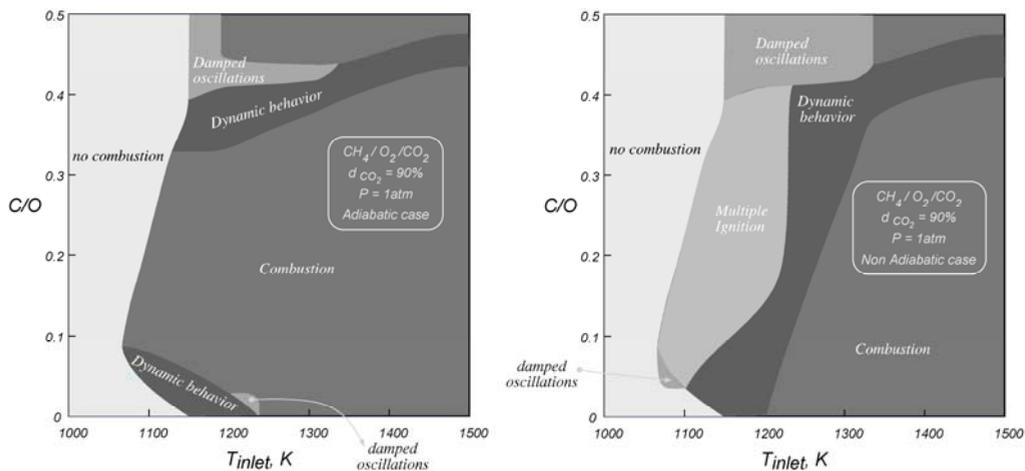


Figure 1. T_{in} -C/O maps for methane mild oxidation in CO_2 dilution.

For the adiabatic case, showed in the left side of figure 1, the region relative to “no ignition” extends from 1000 K up to about 1125 K for all the C/O ratios considered. For all the other C/O and T_{in} conditions, reactive conditions were identified. The widest region of the map corresponds to “steady combustion” area. “Dynamic behaviors” were identified in two different regions of the map. The first zone corresponds to lean ($0 < C/O < 0.1$) and low-intermediate T_{in} ($1070 < T_{in} < 1215$ K) and the second one occurs for fuel rich mixtures ($0.3 < C/O < 0.4$) and inlet temperatures higher than 1150 K. “Damped oscillations” were detected at intermediate inlet temperatures for ultra-lean and very rich conditions.

Figure 2 (right side) shows the ignition numerical map for non-adiabatic conditions. With respect to non-adiabatic systems, also multiple ignitions were numerically identified. They occur from values of C/O equal to 0.05 up to 0.4 and from 1050 K up to about 1200 K. The “dynamic region” marks the shift from the “Multiple ignition” area and the “combustion” regime.

As reported in the introduction, similar oscillation phenomena were detected for steam and N_2 dilution, in non-adiabatic conditions [4, 5, 6, 7]. In such case, it was found that the temperature oscillations were thermo-kinetic, influenced by the heat loss towards the surrounding and modulated by CH_3 recombination path present in the methane oxidation.

The presence of carbon dioxide in the combustion system leads to the establishment of temperature oscillations also for adiabatic conditions. In such case, the dynamic behavior observed in a certain range of temperature and composition is only related to kinetic process. Hence, a kinetic analysis was performed in order to evaluate the main kinetic paths responsible of such phenomena. On the basis of literature suggestions [2, 4, 5, 6, 7, 10, 11], the role of

CO_2 equilibrium inter-conversion reaction ($\text{CO}_2 + \text{H} = \text{CO}_2 + \text{OH}$) and CH_3 recombination ($\text{CH}_3 + \text{CH}_3 + \text{M} = \text{C}_2\text{H}_6 + \text{M}$) on temperature oscillations phenomena was investigated. In particular it was shown that CO/CO_2 equilibrium inter-conversion represents the main reaction of methane oxidation scheme in which CO_2 participates. This reaction competes for H atoms consumption with the chain-branching reactions $\text{H} + \text{O}_2 = \text{OH} + \text{H}$ and $\text{H} + \text{HO}_2 = \text{OH} + \text{OH}$, altering the O/H radical pool, on which the whole reaction process depends. It also competes with the hydrocarbons H-abstraction reaction decreasing paraffin consumption rate. In figure 2 typical temperature profiles related to dynamic behavior of methane oxidation process are reported.

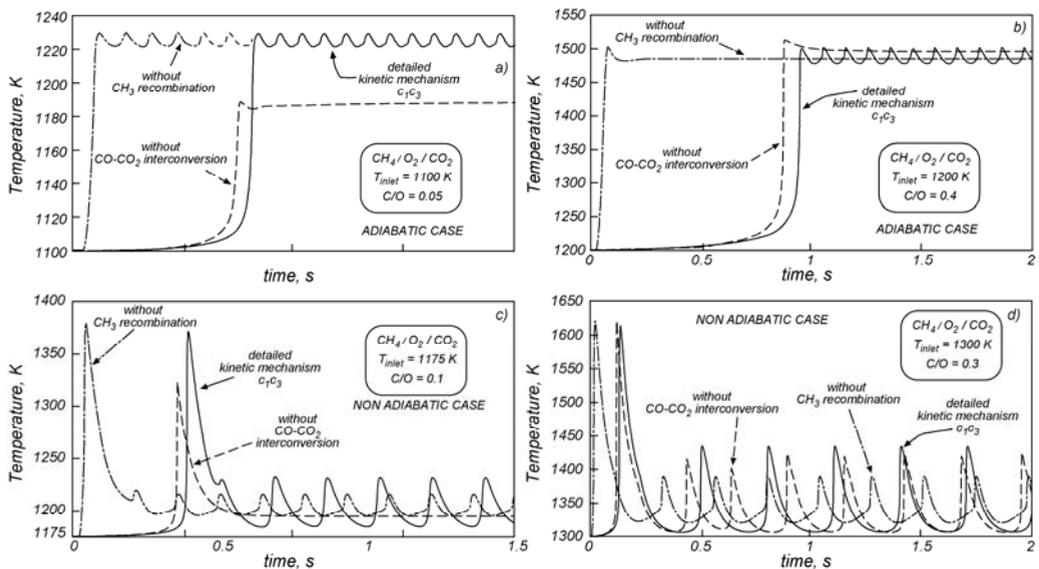


Figure 2. Temperature profiles for adiabatic and non-adiabatic case obtained for different mixture compositions and inlet temperatures by original and modified detailed kinetic mechanisms.

Such profiles, evaluated in adiabatic and non-adiabatic conditions, are computed with the total kinetic detailed scheme and with modified schemes, where CO/CO_2 equilibrium inter-conversion and CH_3 recombination reaction were removed from the detailed kinetic mechanism.

Figure 2 a) shows the temperature temporal profiles for a lean mixture ($\text{C}/\text{O} = 0.05$) pre-heated up to 1100 K in adiabatic conditions obtained with the original and modified mechanisms. In case of c1-c3 detailed mechanism, system shows a first increase of temperature followed by a steady state condition with oscillations. Deleting from the mechanism the CO/CO_2 equilibrium inter-conversion temperature oscillations are not observable, Furthermore, temperature maximum value is lower with respect to the case obtained with the original mechanism. Such

aspect suggests that CO/CO₂ equilibrium inter-conversion plays a key role in the establishment of the dynamic behavior. On the contrary, removing CH₃ recombination, oscillations phenomena are still present. In such case, frequency, amplitude and shape of temperature oscillations do not change significantly with respect to original case. Furthermore ignition process becomes faster.

Different considerations apply for case b). It is relative to a rich mixture characterized by a C/O feed ratio equal to 0.4 and $T_{in} = 1200$ K in an adiabatic reactor. In such a case, the original mechanism predicts a dynamic behavior. No oscillations were numerically observed removing the CO/CO₂ equilibrium inter-conversion or the CH₃ recombination reaction from the c1c3 kinetic mechanism. Such results imply that both the reactions are important for the onset of oscillation phenomena. Also in this case, CH₃ recombination reaction delays the mixture auto-ignition time.

Figure 2c) and 2d) are relative to non-adiabatic cases. It is worth noting that the oscillations are very different from the previous cases and the working averaged temperatures are lower because of heat exchange towards the surroundings.

Figure 2c) shows the temperature temporal profiles in case of a lean mixture (C/O = 0.1) and $T_{in} = 1175$ K in a non-adiabatic reactor. It is possible to note that without CO/CO₂ equilibrium the temperature oscillations disappears, while without CH₃ recombination oscillations remains but they show a different frequency, amplitude and shape with respect to the original case.

In case d) (C/O = 0.3, $T_{in} = 1300$ K, non-adiabatic reactor), the evaluated temperature profile obtained with the mechanism without CO/CO₂ is very similar to the original case. Therefore, the CO/CO₂ equilibrium inter-conversion is not a key reaction for the establishment of oscillations phenomena. Whether the CH₃ recombination path is deleted from the original kinetic mechanism, the temperature oscillation changes significantly in amplitude and frequency.

In adiabatic conditions, for both fuel lean and rich mixtures, the CO/CO₂ equilibrium is a key reaction for the insurgence of the dynamic behavior, as well as in non-adiabatic conditions and for lean mixtures. In mixture rich conditions, for both adiabatic and non-adiabatic conditions, the CH₃ recombination path modulates oscillations amplitude and frequency.

Conclusions

Numerical simulations of oxidation process of methane/oxygen systems highly diluted in CO₂ in a perfect stirred flow reactor were performed. Adiabatic and non-adiabatic conditions were considered.

During numerical analysis, dynamic behaviors were observed for both adiabatic and non-adiabatic case. In adiabatic case, kinetic analysis has shown that temperature oscillations are kinetic-driven and the CO/CO₂ equilibrium inter-conversion and CH₃ recombination path play a key role in the establishment and in the modulation of such phenomena. In case of non-adiabatic systems, temperature

oscillations are thermo-kinetic and they are influenced by the heat loss towards the surrounding.

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