

EFFECT OF DILUENTS ON METHANE OXIDATION IN A JET STIRRED FLOW REACTOR

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Abstract

Advanced combustion technologies, such as MILD, LTC (Low Temperature Combustion) reduce emission of pollutants by controlling system working temperatures to values not critical to promote the formation of several classes of pollutants. To access this temperature range, a significant dilution of reactants is required. At the same time, reactants have to be preheated to sustain the oxidation process. Such conditions are achieved by a strong recirculation of exhaust gases. Such a strategy implies that high contents of CO₂ and H₂O interact with reactants oxidation chemistry. In order to characterize this aspect of the combustion processes under diluted conditions, experimental tests were carried out for methane/oxygen mixtures in presence of N₂, CO₂ and H₂O in a quartz Jet Stirred Flow Reactor (JSFR), at atmospheric pressure, over the temperature range 790-1215 K, from fuel lean to rich conditions and at a residence time of 0.5 s. Temperature and species concentration measurements suggest that the oxidation of methane may be significantly altered by CO₂ and H₂O in dependence of mixture inlet temperatures and equivalence ratios.

Numerical analyses were performed to explore the interaction of diluents with the oxidation chemistry of methane. Results suggested that such species alter the main radical branching mechanisms, i.e. in termolecular reactions as a third body species with high collisional efficiency or directly participating in bimolecular reactions.

Introduction

Diluted combustion strategies (MILD, LTC, etc.) are receiving increased attention as means to reach the needs of efficiency, energy distribution and fuel flexibility, as the resulting peak flame temperatures are low to promote the NO_x and soot formation. To access this temperature range, significant dilution as well as preheating of the reactant mixtures is required. In practical systems, dilution and preheating are usually achieved through internal or external exhaust gas

recirculation [1]. Under highly diluted conditions with intense preheating, the combustion process is expected to have different characteristics [2,3] with respect to conventional fuel-air combustion. Furthermore, the alteration of the combustion properties in diluted systems is stressed by the presence of great amounts of carbon dioxide and steam, induced both by the strong recirculation of exhausted gases towards the fresh reactants and by the use of Low Calorific Value (LCV) fuels. As matter of fact, such species may (1) vary the transport and thermal properties of the mixture, (2) enhance the radiation heat transfer and (3) chemically interact with the oxidation kinetics. These effects occur simultaneously and are intimately coupled [4].

Given this background, the objectives of the current work were to investigate the effect of diluents on the concentration profiles of chemical species, including data obtained in a JSFR, at conditions relevant to diluted combustion. The experiments were carried out for lean, stoichiometric, and rich mixtures, diluted with N₂, CO₂ and H₂O, at atmospheric pressure. The study focused on low-intermediate temperature conditions of practical interest to diluted combustion applications. Methane was chosen as the reference fuel. In addition, numerical analyses were performed to gain an understanding of the contribution of these non-conventional conditions on the combustion chemical kinetics.

Experimental and numerical tools

The oxidation of methane was studied in a JSFR. The system is described in detail elsewhere [3]. The reactor consists of a quartz sphere of 113 cm³. The main flow is composed of oxygen and diluent. It passes through a quartz tube located within two cylindrical electrically heated ceramic fiber ovens. It subsequently mixes with the secondary flow, composed by fuel and diluent, in a premixing chamber. Then the pre-mixed mixture enters the reactor through four nozzles of 1 mm diameter located at its center.

Experiments are performed at constant pressure of 1.1 atm, a constant residence time of 0.5 s, over the temperature range 790-1215 K. Three equivalence ratios (Φ = 1.5, 1, 0.5) were considered and mixtures were diluted with N₂ (reference case) and N₂-CO₂ mixtures or N₂-H₂O mixtures, keeping a fixed overall dilution (d) of 90%.

To provide a detailed chemical analysis, the outlet stable species were analyzed by gas chromatography. To detect and follow accurately the temperature changes during gaseous reactions, a type R thermocouple (40 μ m bead size) was used.

The experimental results obtained in the JSFR were simulated using the PSR code of the OpenSMOKE++ framework [5]. A recently updated detailed gas-phase chemical kinetic model was used, namely the “CRECK-2014” [6].

Results and discussion

Figure 1 shows the experimental evolution of CH₄, CO, H₂, and O₂ concentrations when, starting from a system fully diluted in N₂ at 90%, the CO₂ molar fraction is

gradually increased from 0 to 0.9 (therefore up to a system fully diluted in CO₂ at 90%) and the water vapour molar fraction is increased from 0 to 0.405 for a lean mixture ($\Phi = 0.5$) at $T_{in} = 1180$ K, keeping the overall dilution at 90% (the remaining is nitrogen). This inlet condition has been chosen because it allows for a comparison of the different diluents without the presence of oscillatory regimes.

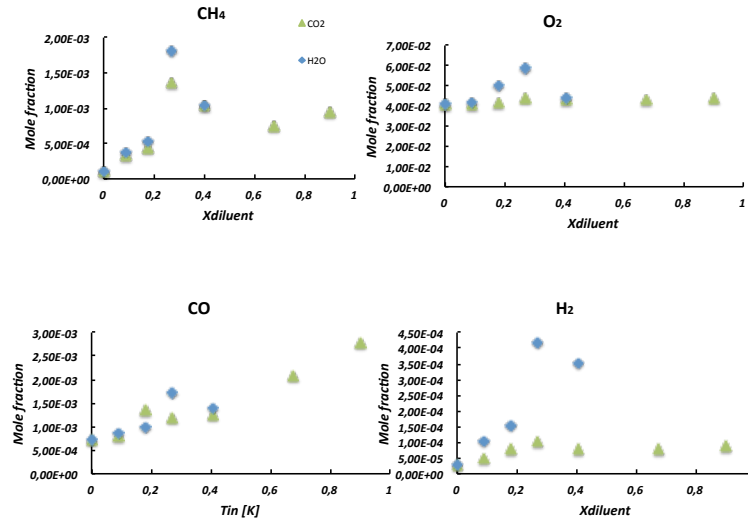


Figure 1. Experimental concentration profiles versus molar fraction of diluent. $\Phi = 0.5$, $\tau = 0.5$ s, $p = 1.1$ atm, $d = 90\%$, $T_{in} = 1180$ K, CO₂ (triangle symbols), H₂O (square symbols).

However, it has not been possible to make a comparison with the numerical results, since the model predicts dynamic regimes for the N₂ and CO₂ diluted systems for this inlet temperature. It is interesting to observe that the conversion decreases quasi-linearly when the CO₂ and steam molar fractions are increased up to a certain value ($X = 0.27$). For higher molar fractions the measured values slightly decrease and then reach a plateau. The only exception is found in the CO concentration, which as the other species reach a plateau level, but it starts again to increase for CO₂ molar fraction higher than 0.405. The slope (in absolute value) of the quasi-straight line defined by the experimental data is found to be slightly higher for the H₂O diluted system than one associated with the CO₂ diluted system.

First of all, this result suggests that CO₂ and H₂O have a significant chemical effect. In fact, any change of a physical property due to the addition of a different species would be proportional to the concentration of that species, and therefore would result in a linear variation in the concentrations of the measured chemical species. As a second consideration it is possible to see that water has a greater

impact than CO₂; indeed small percentages of water are sufficient to obtain large variations in the measured chemical species profiles.

Several kinetic analyses were performed with the aim to understand the interference of CO₂ and H₂O on the oxidation kinetics at stable and steady state conditions.

In particular Fig. 2 shows the evolution of the simulated molar fraction of CH₄ and CH₃, OH, H, HO₂, and O radicals when the CO₂ and H₂O percentage is increased from 0 to 100%, for a stoichiometric mixture at $T_{in} = 1075$ K and $d=90\%$. Therefore in Fig. 2, 0% on the abscissa means that the mixture is diluted at 90% in nitrogen, while 100% means that the mixture is diluted at 90% in CO₂ or in H₂O. All the intermediate dilution levels correspond to mixtures simultaneously diluted in N₂ and CO₂ or N₂ and H₂O in different proportions. $T_{in} = 1075$ K has been chosen because it represents the onset of reactivity and therefore the combustion temperature is the same for all the mixtures, i.e., $T = T_{in}$. This allows focusing attention only on the chemical effects, thus excluding the thermal effect. Furthermore, this inlet condition avoids the presence of oscillatory regimes.

Depending on the CO₂ or H₂O molar fraction, the presence of these two molecules leads to changes in the production and in the consumption of stable species and radicals. Note that the trend observed for the CH₄ as a function of diluent percentage is similar for all the other stable species. It is important to note that relatively small quantities of CO₂ and H₂O are required to have significant changes on the chemical species concentrations. The conversion and the total radical pool decrease quasi-linearly when the CO₂ and H₂O molar fractions are increased up to a certain value. Further increase of the CO₂ or H₂O concentration does not lead to proportional changes observed so far. In particular the plateau is reached for a CO₂ percentage of about 60% and a H₂O percentage of about 30%. This may indicate that chemical effects of CO₂ addition are lower than the chemical effects related to H₂O addition.

Several kinetic analyses were performed with the aim to understand the nature of these phenomena. The results suggest that this behaviour is attributed to the role of the methyl radical recombination reaction ($CH_3 + CH_3 + M = C_2H_6 + M$) in affecting the chain branching. As a matter of fact, interestingly, the reactivity, expressed as methane mole fraction in fig. 3, behaves qualitatively similar to the rate of recombination reaction as a function of the diluent percentage.

This is reasonable because with increasing CO₂ or H₂O content the influence of three-body reaction first increases. Then, the recombination reaction moves from the low-pressure limit toward the high-pressure limit reducing the third body effect and consequently increasing the reactivity according to the Lindemann mechanism. Therefore, the methyl radical recombination reaction is third-order in the nitrogen dilution and second-order in the CO₂ or H₂O dilution.

Moreover, the relatively lower reactivity in H₂O dilution is mainly due to the reaction $CH_4 + OH = H_2O + CH_3$. The larger presence of water reduces the OH abstraction, slightly moving the thermodynamic equilibrium toward the reactants,

thus decreasing the chain propagation effect. The consequent OH radical concentration increase, observed in Figure 2, is a further confirmation of this statement.

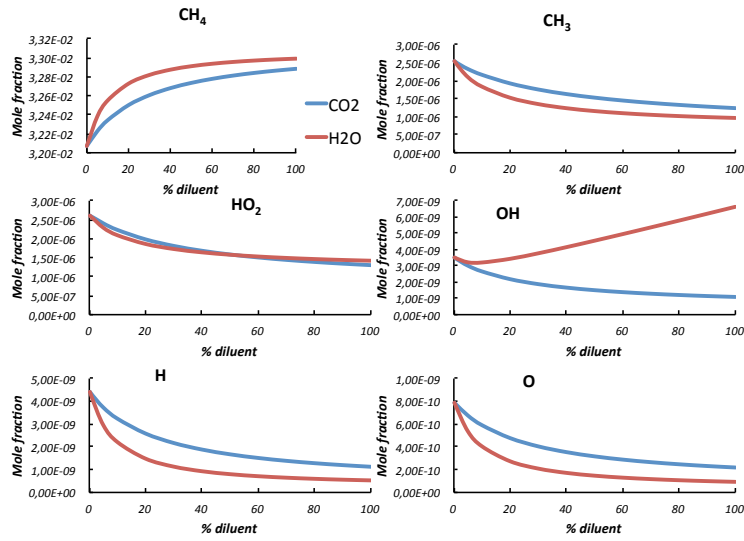


Figure 2. Simulated concentration profiles versus percentage of diluent. $\Phi = 1$, $\tau = 0.5$ s, $p = 1.1$ atm, $d = 90\%$, $T_{in} = 1075$ K, CO_2 (blue lines), H_2O (red lines).

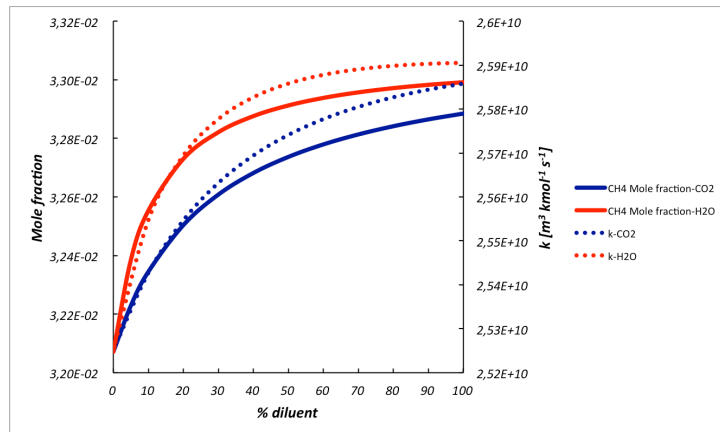


Figure 3. Simulated methane molar fraction (left axis) and rate of methyl radical recombination (right axis) versus the percentage of diluent. $\Phi = 1$, $\tau = 0.5$ s, $p = 1.1$ atm, $d = 90\%$, $T_{in} = 1075$ K, CO_2 (blue lines), H_2O (red lines).

Conclusion

The present work experimentally characterized the oxidation process of diluted and pre-heated methane mixtures, at atmospheric pressure, in a Jet Stirred Flow

Reactor under a wide range of operating conditions involving temperatures, mixture compositions and dilution levels. The diluent gases used were N₂, CO₂ and H₂O. The attention was focused on oxidation characteristics and their dependences on the diluent type.

The influence of diluents was analyzed on temperature and stable species concentrations profiles.

It was observed that the fuel conversion decreases when the CO₂ or water vapour concentration is increased. This decrease is quasi-linear with gradually increasing CO₂ or H₂O molar fraction up to a certain value. Further increasing the CO₂ or H₂O concentration does not lead to proportional changes in the behaviour. This impact is found to be greater in H₂O dilution than in CO₂ dilution.

Given that most of the studies available in the literature on the effects of diluents involved very low concentrations of them, the quasi-linear decrease of conversion with increasing CO₂ and steam molar fractions observed for lower CO₂ and H₂O molar fractions have been used in several work to build semi-empirical models, based on one-step overall reactions. De facto, although based on crude assumptions, these models can be used to quickly estimate the combustion properties of CO₂- and/or steam-diluted fuel mixtures. However, as just demonstrated, careful attention should be paid in the extrapolation of these observations in processes where high concentrations of these species may be present, such as in the case of oxy-fuel combustion. Such an effect would not be captured with a one-step overall reaction. This again highlights the importance of detailed chemistry in modelling such combustion systems.

References

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