

# Study of oscillations during methane oxidation with species probing

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## Introduction

Biogas has been considered as a renewable energy source with respect to fossil fuels due to its sustainability, security supply, and environmental friendly potential [1-4]. Methane occupies a large part in biogas. It is of great value to review the methane oxidation for a primary understanding of the features associated with biogas combustion. It was found that dynamic behavior in terms of methane oxidation occurred under specific conditions. The first methane oxidation oscillation experiments were conducted by [5] in a jet-stirred reactor (JSR) and were extended to a higher inlet temperature [6]. The map of dynamic behavior was drawn in terms of various C/O ratios and temperatures ranging from 1025-1275 K at a fixed 90% nitrogen bath gas. Recently, Lubrano Lavadera *et al.* [7] investigated the main parameters, such as, equivalence ratios (0.5-1.5), residence time (1.5-2 s), various bath gases (N<sub>2</sub>, CO<sub>2</sub>, He, H<sub>2</sub>O), on the oscillatory behavior of methane oxidation. However, to our best knowledge, studies of dynamic phenomenology with species probing have never been reported.

Because of the heat release in terms of the exothermic or endothermic reactions, the temperature and species oscillations are strongly coupled during fuel oxidation. In order to put emphasis on species dynamic behavior, very diluted conditions are needed to decouple as much as possible temperature and species oscillations.

The purpose of this work is to investigate the effects of various parameters: inlet mole fraction of methane (0.1-0.5%), stoichiometric condition ( $\Phi=1$ ) and reactor temperatures (950-1200 K), on the species oscillations during methane oxidation. A detailed kinetic mechanism (POLIMI) [8] is selected to interpret the experimental data.

## Experimental details

The experimental setup was a laboratory-scale spherical fused silica JSR (volume of 85 cm<sup>3</sup>), the detailed description of the setup was provided elsewhere [9]. The reactant gases were pre-mixed in the preheating zone before entering the reactor center through four nozzles, which created high turbulence resulting in homogeneity in composition and temperature of the gas phase. The residence time was fixed to 2.0 s. The reactor temperature was measured by a type-K thermocouple located at the center of the reactor. The pressure in the reactor was controlled by a needle valve positioned at the downstream of the reactor and kept to 800 Torr. Helium, oxygen and methane were provided (purities of 99.9 %, respectively) by Messer and the flow rates of the reagents were controlled by mass flow controllers. In order to measure the temperature inside the JSR reactor, a Pt13%Rh thermocouple (0.2 mm bead size) was inserted inside the reactor, meanwhile, a capillary tube was also placed inside the reactor for sampling species, which were quantified by means of a mass spectrometer calibrated using standard. The uncertainty of the diagnostic instruments were estimated to be  $\pm 20\%$ .

## Kinetic Model

The kinetic mechanism used for chemistry description and analysis of experimental results was adopted by following the POLIMI kinetic framework, describing the pyrolysis and oxidation of hydrocarbon fuels [8]. The core C<sub>0</sub>-C<sub>3</sub> mechanism was modified by coupling the H<sub>2</sub>/O<sub>2</sub> and C<sub>1</sub>/C<sub>2</sub> subsets from Metcalfe et al. [10], C<sub>3</sub> from Burke et al. [11], and heavier fuels from Ranzi et al. [8, 12]. For the low temperature part, particular attention was devoted to updating the (equilibrated) reaction rates of peroxy radical formation from methyl radical [13], along with the corresponding thermodynamic properties. They were adopted, when available, from the database of Burcat and Ruscic [14].

## Results

Experiments for the oxidation of CH<sub>4</sub> with Helium as bath gas were performed under stoichiometric ( $\Phi = 1$ ) conditions over the 950–1200 K temperature range. The experimental conditions are summarized in Table .

Exp.	X <sub>CH<sub>4</sub></sub> [-]	X <sub>O<sub>2</sub></sub> [-]	$\Phi$ [-]
1	0.001	0.002	1
2	0.0025	0.005	1
3	0.005	0.01	1

*Table 1 Experimental conditions. He is used as balance gas.*

In the case of the initial methane mole fraction fixed to 0.1%, no obvious temperature or species oscillations are observed under all the investigated conditions due to too high diluted conditions. In the presence of 0.25% inlet mole fraction CH<sub>4</sub>, at 1175 and 1200 K, under stoichiometric condition, less than 2 K temperature oscillation is detected, i.e., a representative condition, which isolates the temperature oscillations from species oscillations, is achieved. The upper panel of Fig.1, shows the time evolution of mole fraction of CH<sub>4</sub>, O<sub>2</sub> and CO<sub>2</sub> deduced from the mass signals at m/z 16, 32 and 44, respectively, at these two temperature points when the initial methane mole fraction is 0.25%. At 1175 K, an oscillation frequency of 0.0495 Hz is observed with all these three tracked species. As the temperature increases to 1200 K, the dynamic behaviors become more intense with a frequency of 0.124 Hz, which indicates that the oscillation regime is very sensitive to the temperature with respect to the methane oxidation.

Regarding to the methane initial mole fraction fixed to 0.5%, two selected cases are displayed in the bottom panel of Fig.1, which are at the same temperature points compared to those when the initial methane mole fraction is 0.25%. Note that the temperature and species oscillations are also observed even at 1150 K with the presence of 0.5% methane, which implies that the higher amount of methane extends the temperature range where oscillations are observed. When the temperature is 1175 K, the amplitude of the temperature oscillations is again approximately 2 K. The species fluctuations exhibit a frequency of 0.182 Hz. Compared to those with inlet composition methane 0.25%, the oscillation frequency becomes faster with methane mole fraction 0.5% at 1175 K. As the temperature further increases to 1200 K, a more severe dynamic behavior are obtained with a frequency of 0.341 Hz.

From the model point of view, there is a general good agreement between the experimental data and simulated results. The model could reasonably capture the frequency of the dynamic behavior in all the cases, although the model overestimates the amplitude of the species oscillations at 1200 K.

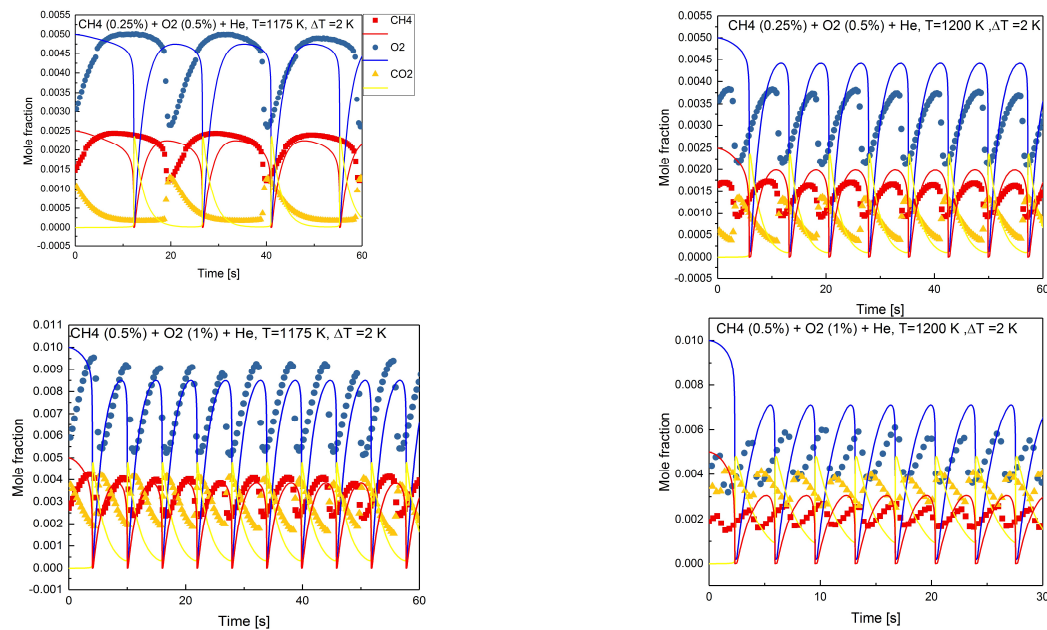


Figure 1. Comparison between experimental species profiles (symbols) and modeling predictions (lines) in the methane oxidation with inlet mole fraction 0.25-0.5% CH<sub>4</sub>, 0.5-1% O<sub>2</sub>, T=1175-1200 K, phi=1. (He as balance gas).

## Conclusions

Investigations associated with the dynamic behaviors during methane oxidation were performed under high diluted conditions with species probing. Experiments were carried out in a Jet-stirred reactor temperatures ranging from 950-1200 K, with inlet methane mole fractions (0.1%-0.5%), at a fixed residence time 2 s, under stoichiometric conditions. POLIMI kinetic model was employed to interpret the experimental data in terms of oscillation. It was found that the oscillations occur at relatively high temperature (1175-1200 K) under stoichiometric condition with high dilution. The dynamic behavior become more intense when temperature and the initial methane mole fraction increase. The model can reproduce well the experimental data, especially for the frequency of oscillation.

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