COMPUTER MERHODS IN COMBUSTION

Report

LIFESPAN OF HYDROXYL RADICALS IN AIR-METHANE MIXTURES

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Contents

1 Abstract

A study have been conducted, to research the lifespan of hydroxyl molecules in methane-air kinetic combustion reaction. A Python-based, numerical, Cantera model of a zero-dimensional flow reactor was used.

2 Introduction

2.1 Purpose

The simplest stable, naturally occurring hydrocarbon within close reach on Earth is Methanol. That is why it is very popular fuel used for thermal energy production. No other aliphatic hydrocarbon, with LHV of 50 MJ/kg of CH4 can produce more energy than methane during the stoichiometric reaction of a unit mass of methane combustion.

CH4 + 2O2 - CO2 + 2H2O (890,32 kJ/mol)

Because of extensive reactions taking place in the same time to convert methane into carbon dioxide, water vapor and many other less desired byproducts are produced. These reactions generate many types of compounds such as ions and free radicals, which are very reactive in non-extreme combustions. In spite of the fact that their nature is transitional and concentrations are little, their role in combustion process is crucial.

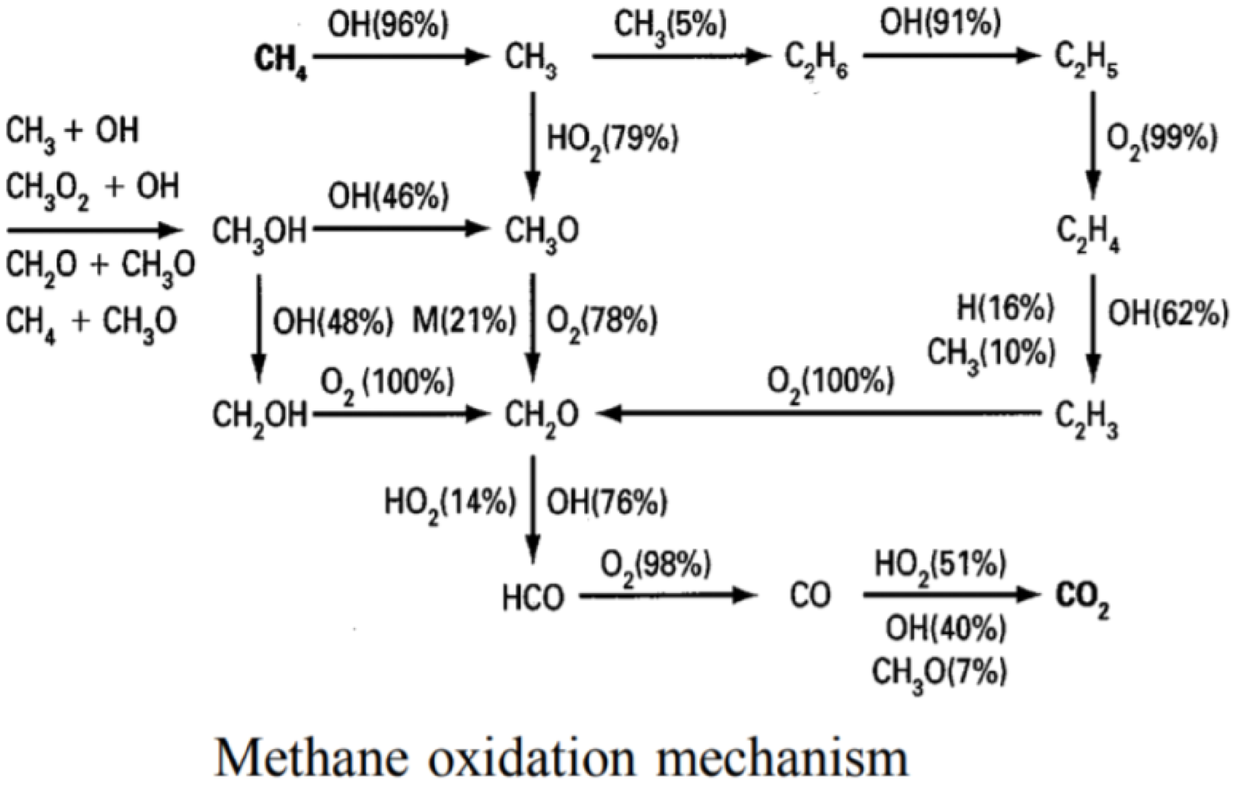

Figure 1: Methane oxidation mechanism scheme showing complexity of reaction

2.2 Methods

Firstly, electric spark ignites premixed fuel and air - thanks to that the energy which is introduced into gas makes it dissociated. The chain reaction starts, and hot gas, which is the "activator" sets surrounding mixture ablaze along with vivid chemical reactions. It is known, that heating medium is not only heating up the mixture before it, but also diffusely introducing free radicals to the flame. Hydrogen and hydroxyl to name a few, only when the flame's propagation velocity is sufficiently slow. OH - species can by detached in entire reaction volume after peaking in the most heated area. Slowly recombining with other radicals unless these products cool down. This process which usually takes time as recombination of two radicals is too exothermic for reaction product to remain stable, demanding less probable third particle assistance with excess energy dissipation. Miscellaneous procedures can be utilized to detect free radicals inside the flame. Lot of techniques can be used like Laser Induced Fluorescence (LIF) to define concentrations of the species. After laser pulse excitation of a burning gas and measurement of UV light emission intensity about 300 nm, range of high OH radical concentration can be localized, thus it makes possible to find flame front and the chemical reaction area. If radical persist in reaction mixture for longer, the longer combustion takes place. It could be the most important for proper operation of furnaces, piston engine or thermobaric explosives that rely on accurate prediction of a reaction time. Making the simulation using Cantera software, concentration of hydroxyl radicals and their "time of life" in reaction mixture were determined.

The numerical calculations were performed by the different equivalent ratios, which is by definition:

$$\Phi = \frac{\text{Amount of air theoretically needed for combustion}}{\text{Amount of air provided}} \tag{1}$$

3 Results

3.1 Charts

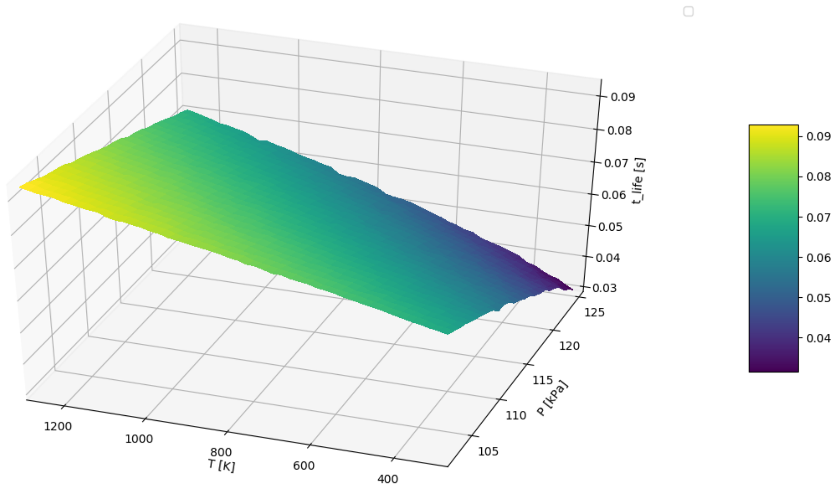

Figure 2: Lifespan of hydroxyl radicals $\Phi = 0,1$.

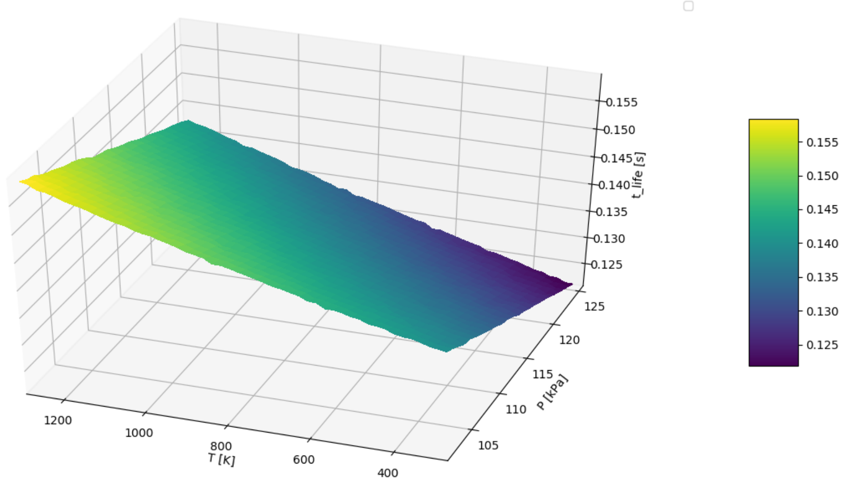

Figure 3: Lifespan of hydroxyl radicals $\Phi = 0,2$.

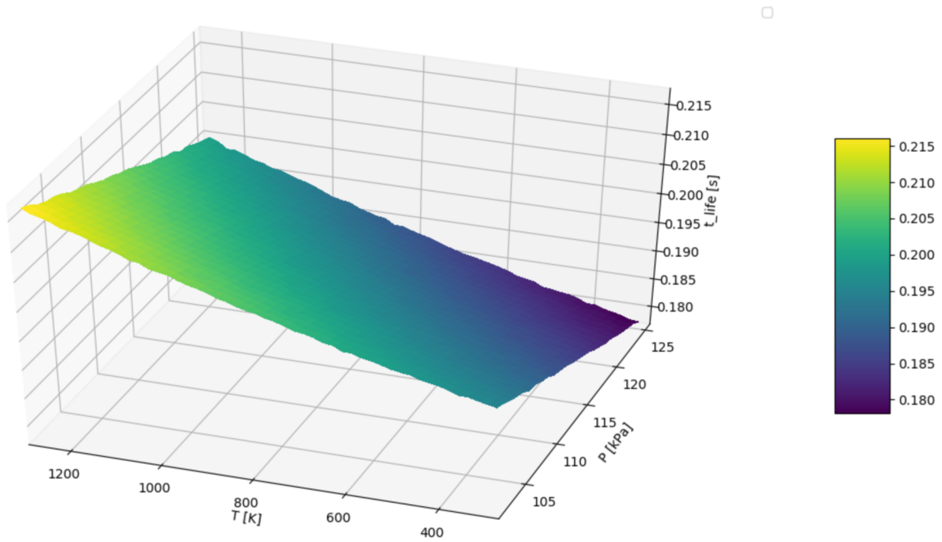

Figure 4: Lifespan of hydroxyl radicals $\Phi = 0,3$.

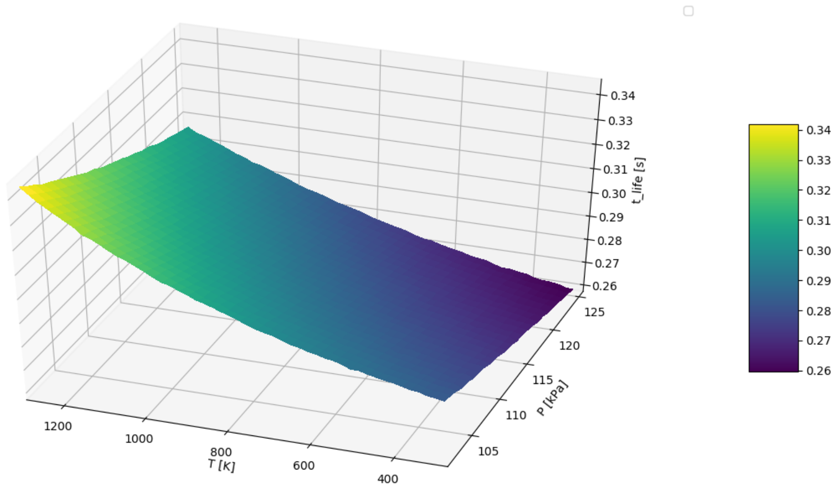

Figure 5: Lifespan of hydroxyl radicals $\Phi = 0,5$.

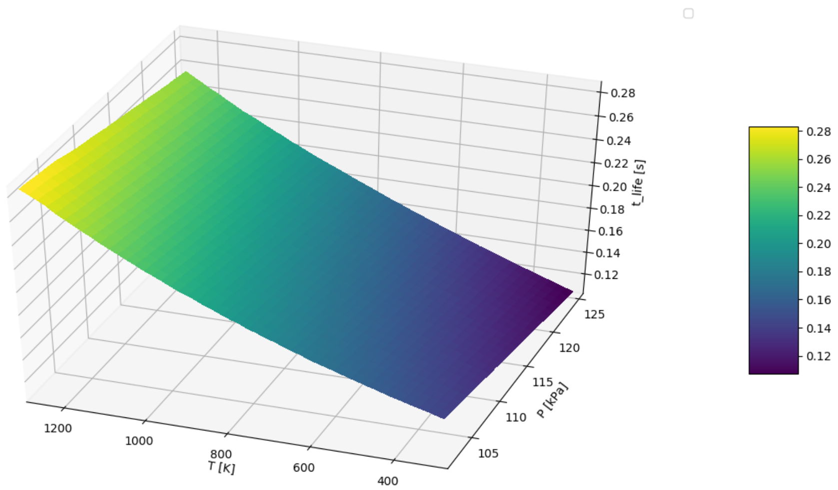

Figure 6: Lifespan of hydroxyl radicals $\Phi = 1,5$.

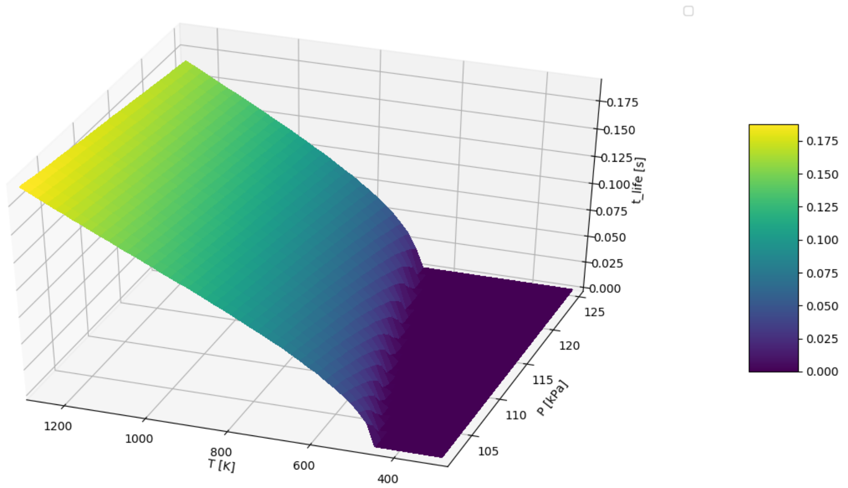

Figure 7: Lifespan of hydroxyl radicals $\Phi = 1,6$.

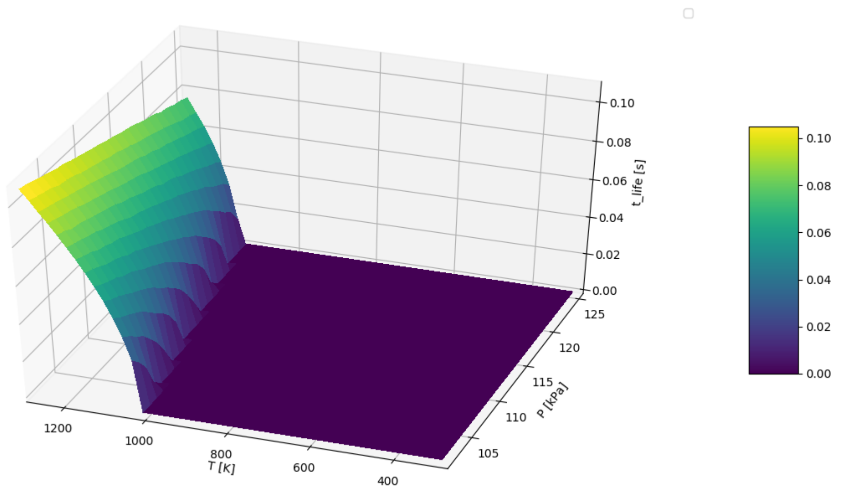

Figure 8: Lifespan of hydroxyl radicals $\Phi = 1,7$.

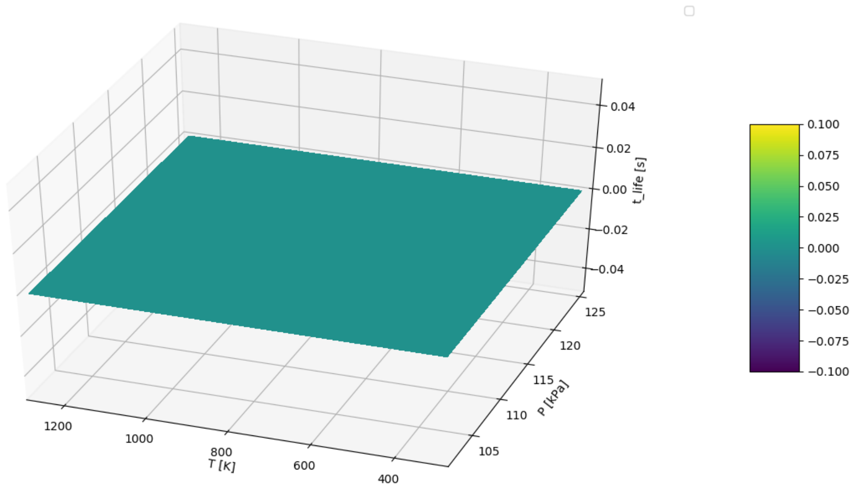

Figure 9: Lifespan of hydroxyl radicals $\Phi = 1,8$.

3.2 Analysis

Cases were enumerated for easier identification process:

1. $\Phi = 0,1$
2. $\Phi = 0,2$
3. $\Phi = 0,3$
4. $\Phi = 0,5$
5. $\Phi = 1,5$
6. $\Phi = 1,6$
7. $\Phi = 1,7$
8. $\Phi = 1,8$

Cases 1-4 (Fig. 2.-Fig. 5.) have generally less fuel in the mixture, thus they are called lean mixtures. With growth of equivalent ratio the lifespan of hydroxyl radical increases. For cases 5-8 (Fig.6-Fig.9.), which are rich mixtures, an opposite trend is observed. Lifespan decreases with higher equivalent ratios. Additionally, flat surfaces are present on charts shown Fig. 7. - Fig. 8, this means there was no reaction until some temperature rise. Also, higher pressure has detrimental effect on flammability. Temperature means more energy of the molecules, thus better probability of molecules bumping into each other and reacting, however pressure has damping effect. Figure 9 shows completely flat surface, which means the mixture is too rich, over the methane flammability limit.

The longest lifespan occurs for $\Phi = 0,5$ noting 0,34 second. Analysing all cases, there is a visible conclusion: longer lifespans occur with air to fuel ratios closer to stoichiometric.

4 Summary

Hydroxyl radicals are surely inseparable part of methane combustion in air. They are very reactive and quickly disappear in further reaction. A simple Cantera combustion model showed how the quality of mixture can affect the time of existence of hydroxyl radicals. Their lifetime ranges up to a third of a second for equivalent ratio equal to 0,5. Although, it must be remembered, that model is still far from reality.

List of Figures