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Project of Cantera Computer Methods in Combustion

THE LIFESPAN OF HYDROXYL RADICALS
IN AIR - METHANE MIXTURES

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Warsaw 2019

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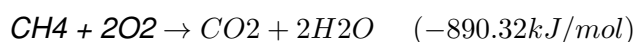
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1 Abstract

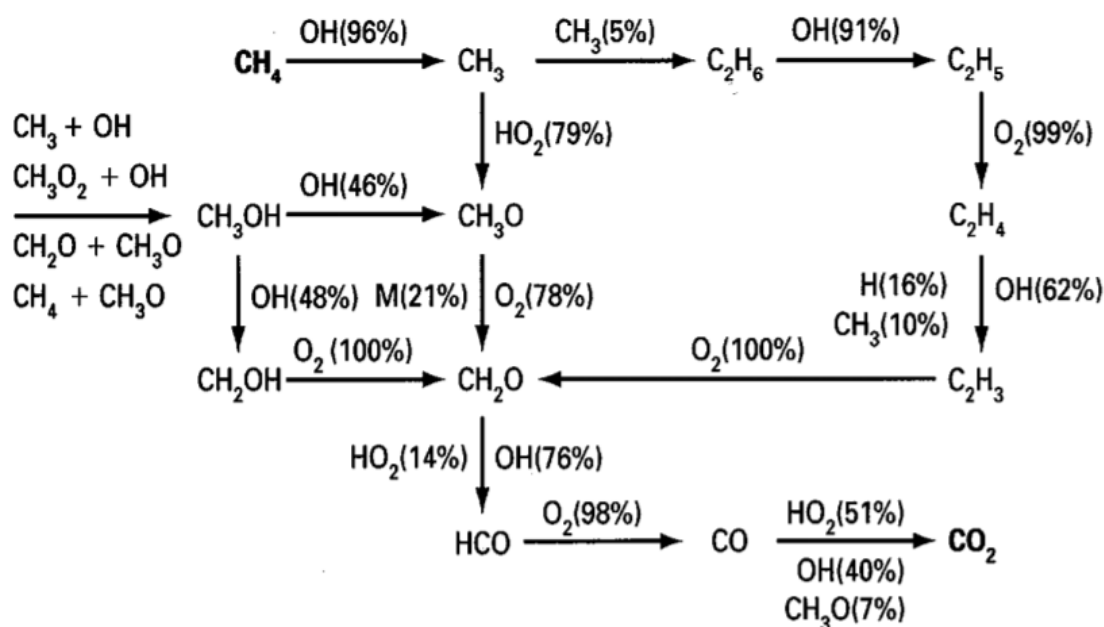
Given research summarises computational studies of hydroxyl radicals time of presence inside a numerically modelled, non-dimensional flow reactor. Kinetic combustion of methane – air mixtures were studied with varying fuel to air proportions, initial pressures and temperatures. Results were presented and discussed.

2 Introduction

Methane is the simplest stable, naturally occurring hydrocarbon. Readily available on Earth, it constitutes one of most popular fuels used for thermal energy production and propulsion. Stoichiometric reaction of a unit mass of methane combusted in the air releases more energy than any other aliphatic hydrocarbon, with LHV of 50 MJ/kg of CH₄.



Combustion of methane in the air is a complex phenomenon, as multiple reactions are taking place simultaneously to convert methane into carbon dioxide, water vapor and other, usually less desired by-products. These reaction paths generate in situ wide variety of compounds, for instance ions and free radicals, which are very reactive in non-extreme conditions. Despite their transient nature and minute concentrations, their role in combustion process is crucial.



Methane oxidation mechanism

Figure 1: Methane – oxygen reaction graph with some major side reactions presented. According to experimental studies, CH₄ molecules begin their oxidation process by being converted into a radical, usually via interaction with hydroxyl radicals or other species present in the flame [1].

When electric spark ignites fuel premixed with air, the energy introduced into gas renders it dissociated, thus generating radicals and ions. Then a chain reaction starts and hot, “activated” gas sets surrounding mixture ablaze along with vivid chemical reactions. It was discovered, that not only flame heats up the mixture before it, but also diffusely introduces to it free radicals, hydrogen and hydroxyl to name a few [1], provided that the flame’s propagation velocity is sufficiently slow. After peaking in the most heated area, these OH species can be detected in entire reaction volume, slowly recombining with other radicals as the combustion products cool down. This process takes time, as usually recombination of two radicals is too exothermic for reaction product to remain stable, thus requiring less probable third particle assistance with excess energy dissipation. Various experimental procedures can be utilised to detect free radicals inside the flame. Concentrations of the species can be visualised using techniques like Laser Induced Fluorescence (LIF). After laser pulse excitation of a burning gas and measurement of UV light emission intensity around 300 nm, region of high OH radical concentration can be localised and thus – the flame front and the chemical reaction area. The longer radicals persist in reaction mixture, the longer combustion takes place. This might be of paramount importance as proper operation of furnaces, piston engines or thermobaric explosives rely on accurate prediction of a reaction time. During simulations, performed using Cantera software, concentration of hydroxyl radicals and their “time of life” in reaction mixture were determined.

3 Models

Our model is based on example attached to Cantera 2.3 documentation. Reaction is simulated in zero dimensional space (the main outcome of this assumption is neglect of thermodynamical parameters' spatial distribution). It consists of four gas containers, two of which are reservoir type and their purpose is to serve as sources of flowing gas. Reservoir object types are respectively methane and air containers. Then there is a flow reactor type container, filled with pure nitrogen in the beginning. Then, as simulation advances in time, methane and air streams enter the reactor and mix themselves together. The fourth container is source of H radicals stream, which is simple model of spark ignition used for zero dimensional simulations. To make circulation of gas possible in reactor, an exhaust with a valve is attached. They're modelled by premade objects from Cantera library. Valve helps maintain constant pressure of gas escaping the reactor. A set of starting conditions is applied to each container. Conditions are: temperature, pressure and equivalence ratio of methane-air mixture (determined by values of their mass flow rates). Function „step()” is used to iterate solution over time. It uses adaptive time step, refined with rise of gradients of main properties, in order to correctly capture dynamics of whole process. Outcome report of simulation contains values of OH radical lifespan, maximum OH mass fraction and set of starting conditions to help identifying results. They're held in Python list type objects. Method to evaluate OH radical lifespan is based on capturing time frames when it's mass fraction value exceeds given minimum value, marked as „epsilon”. Knowing that simulation is iterated over arbitrarily set time frame, a risk of results being dependant on that time occurs. It can happen, when OH mass fraction is higher than epsilon while reactor reaches steady burning condition. If then calculation process is upheld for some extra time, this extra time becomes added to actual OH radical lifespan. To avoid this, we added algorithm checking whether current mass fraction in time derivative is constant and if current value of mass fraction is lower than maximum value as for now. Providing both of these conditions are true, simulation is stopped immediately to freeze number on lifespan counter and thus keep solution correct.

4 Results

4.1 Lean mixtures

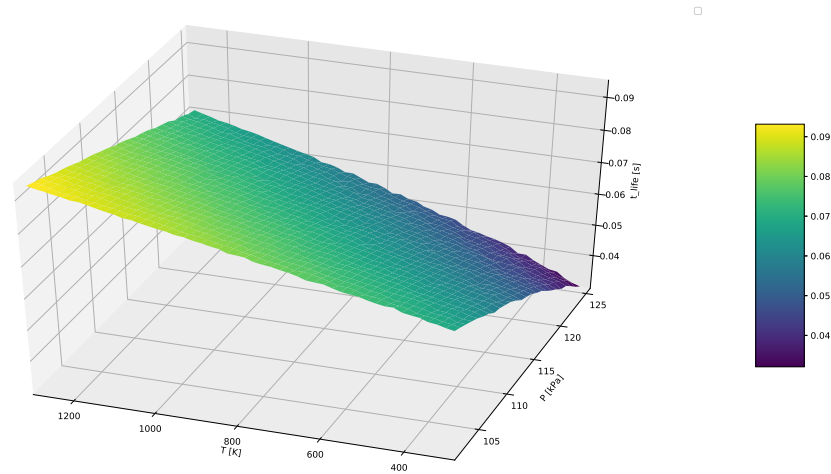


Figure 2: The lifespan of hydroxyl radicals with equivalent ratios 0.1

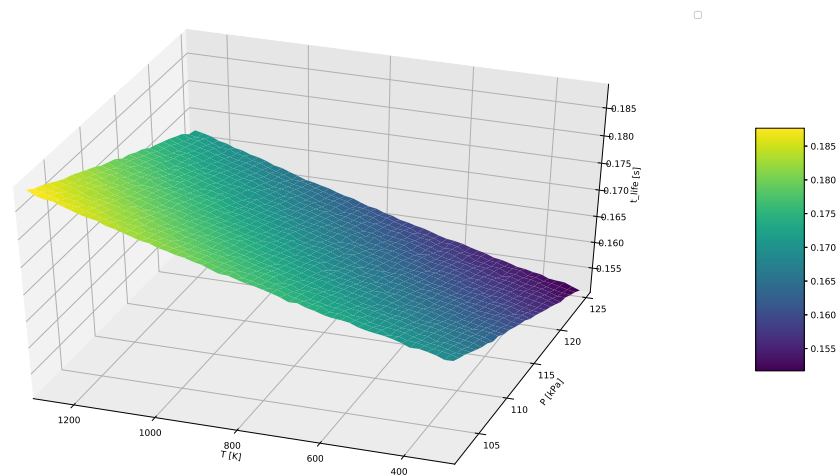


Figure 3: The lifespan of hydroxyl radicals with equivalent ratios 0.2

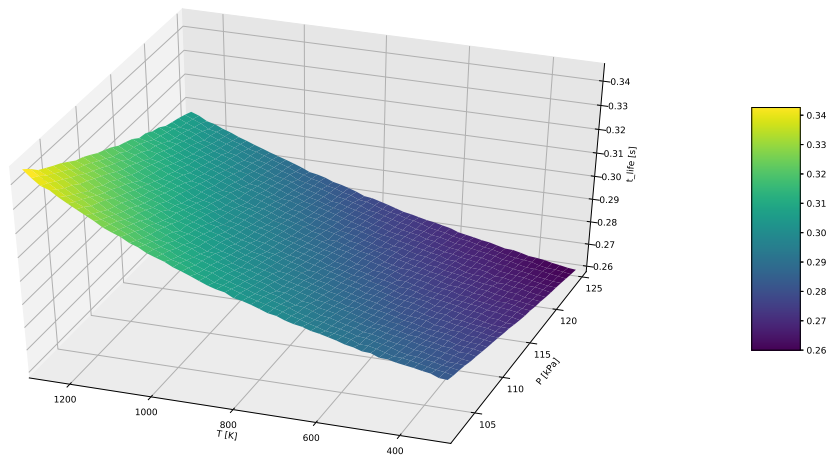


Figure 4: The lifespan of hydroxyl radicals with equivalent ratios 0.5

4.2 Rich mixtures

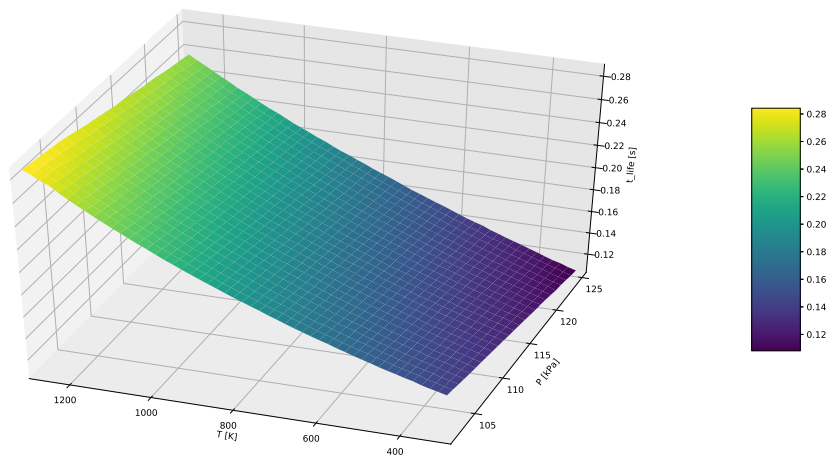


Figure 5: The lifespan of hydroxyl radicals with equivalent ratios 1.5

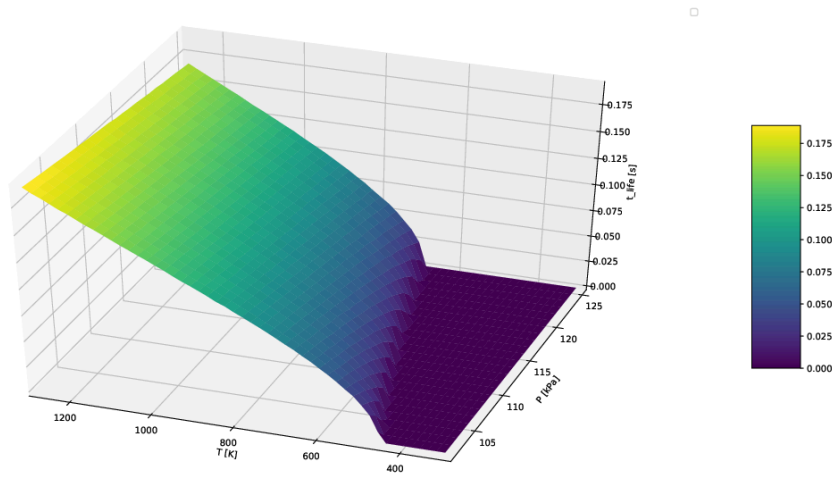


Figure 6: The lifespan of hydroxyl radicals with equivalent ratios 1.6

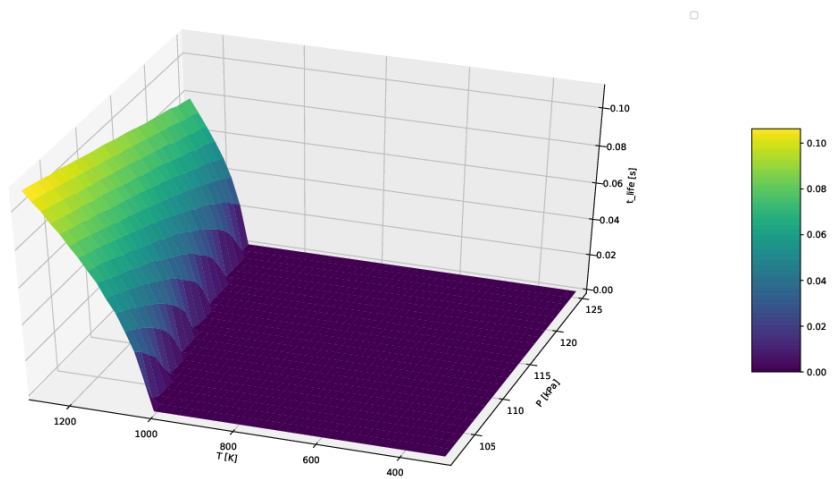


Figure 7: The lifespan of hydroxyl radicals with equivalent ratios 1.7

5 Summary

Computed lifespan of free hydroxyl radicals, depicted in the graphs Figure 2 – 7, is very short, ranging from few up to several milliseconds, and stands with good comparison with experimental results. It is the consequence of high reactivity of these species – they tend to react with other compounds present in a mixture really quickly to form new radicals or to recombine with each other. Depending on the equivalence ratio, calculated OH lifespan can vary by an order of magnitude. It was observed to elongate with mixture proportions getting closer to stoichiometric composition, as the production and concentration of these radicals peaks at this point. Moreover, for rich mixtures, reaction takes place only in specific range of pressure and temperature combinations. It is strictly connected with methane's flammability limits.

Independently of air's excess over fuel, span of their existence extends itself with rise of temperature. Higher temperature implies higher value of molecules' kinetic energy, leading to higher probability of molecule's splitting into atoms. On the other hand, rise of the pressure suppresses molecules' ability to dissociate in both homo- and heterolithic way, apparently accelerating combustion reaction as well.

In engineering-natured calculations, time of approaching to chemical equilibrium is treated as negligible. In our work, we determined scale of error generated when committing to that method. It is vital to mention, our calculations are merely approximation of reality. A simple numerical model was used, which approximates the value basing on arbitrarily assumed "epsilon", a limit of radicals' meaningful presence in the mixture.

References

- [1] W. E. Wilson, Jr., R. M. Fristrom *Radicals in Flames*. APL Technical Digest, July – August 1963;
- [2] Graph 1 source: University of Toronto Institute for Aerospace Studies, lectures on Combustion and Propulsion by O. Gulder.
- [3] Model of combustor: [cantera.github.io](https://github.com/Cantera/cantera);