Project in Cantera
Computer Methods in Combustion

The lifespan of hydroxyl radicals in air-methane mixtures

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1 Introduction

Methane (CH_4) is one of the most popular fuel appearing in gas state, in normal conditions. It is the simplest, stable hydrocarbon, naturally occurring and available on Earth. Stoichiometric reaction of a unit mass of methane combusted in air gives more energy than any other aliphatic hydrocarbon, that's why it is used for thermal energy production and propulsion. Combustion methane-air mixture is a complex phenomenon, as many reactions are taking place to convert methane into carbon dioxide, water vapor and other side products. Wide variety of compounds like ions and free radicals are generated by these reactions. It is worth noting that despite their transient nature and minute concentrations they play an important role in combustion process.

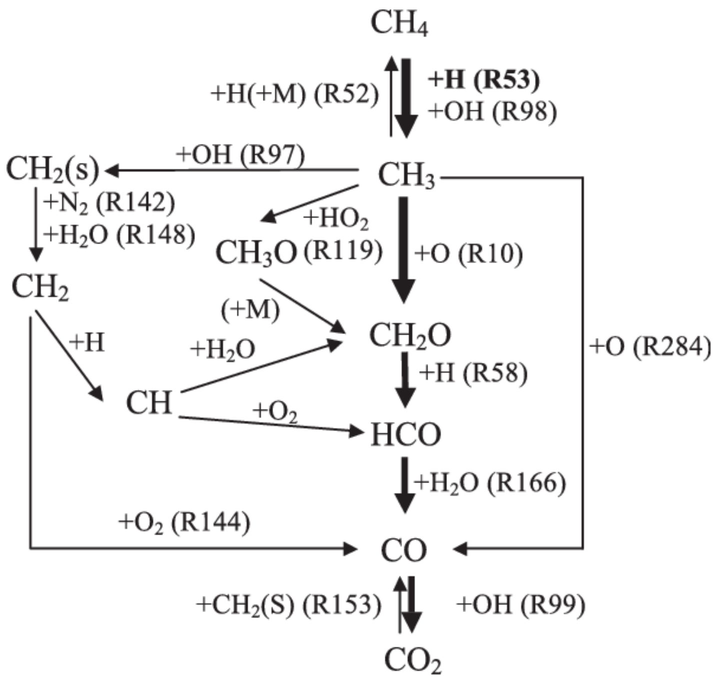

Figure 1: Methane - oxygen reaction graph . CH4 molecules begin their oxidation process by being converted into a radical, usually via interaction with hydroxyl radicals or other species present in the flame.

Gas is rendered dissociated, by the energy from premixed fuel with air ignited by electric spark thus it generates radicals and ions. Next, a chain reaction starts and hot gas sets surrounding mixture on fire along with intense chemical reactions. It turned out that not only flame heats up the mixture but also before, it introduces free radicals, hydrogen and hydroxyl into the mixture, if only the flame's propagation velocity is sufficiently slow. In the most heated area, these OH species can be detected in the entire reaction volume, slowly connecting with other free radians when the combustion products cool down. This process occurs, as usually recombination of two radians is too exothermic to remain stable for reaction product, thus requiring less probable third particle assistance with excess energy dissipation. To detect free radians in flame various experimental procedures can be used. Laser Inducted Fluorescence (LIF) is a method that can visualise concentrations of the species. After laser send pulse beam into a burning gas, it can measure UV light intensity about 300 nm, the region with high radian accumulation can be localised, thus the chemical reaction area and the flame front. Combustion time is highly dependent of radical lifespan. The longer radicals occur in reaction mixture, the longer combustion takes place. This might be a major importance as proper operation of piston engines, furnaces or accurate predicting of a reaction time in thermobaric explosives. Concentration of hydroxyl radicals and their “lifespan” in reaction mixture were determined using Cantera software.

2 Model

For the simulation of the combustion process, we’ve used model provided by Cantera 2.3. The Cantera model simulates the reaction in zero dimensional space (this assumption neglects thermodynamical parameters spatial distribution). The model describing the combustion consists of four gas containers. Two of them are reservoir type and it’s purpose is to serve as a source of flowing gas. Reservoirs contain methane (CH_4) and air. The third gas container is a flow reactor type container, filled with pure nitrogen (in the beginning). The fourth container is a source of H radicals stream, which is simple model of spark ignition used in sero dimensional simulations. As simulation takes place, methane and air streams enter the reactor and mix. Mixing of gas in reactor is achieved by attaching exhaust with a valve, which is modelled using Cantera library. Valve’s purpose is to maintain constant pressure of gas escpaing the reactor. Based upon the case, a set of starting conditions (temperature,pressure,equivalence ratio of methan-air mixture -determined by the values of their mass flow rates) is applied to each container. The function called ”step()” was used to calculate the solution over time. The function uses adaptive time step, based upon the rise of gradients of main properties, in order to correctly ilustrate the dynamics of process. The result graphs ilustrate the lifespan of OH radicals for different initial conditions.The results are held in list type of objects. Method of evaluating OH radical lifespan is based on capturing the mass fraction value for different time frames and comparing them to given minimum valuve called ”Epsilon”. Given that the simulation is iterated over arbitrarily set time frame, a risk of results being dependant over that parameter occurs.It can happen when OH mass fraction is higher than Epsilon while reactor reaches steady burning condition, which would add extra time to results and falsify them. To avoid this, algorithm checking wheather current mass fraction in time derivative is constant and checking if current value is lower than the maximum value. If both of this conditions fulfilled, simulation is stopped immediately to freeze number on the lifespan couner. This algorithm ensures that the solution is correct.

3 Results

The simulation was dividied into two parts based upon the equivalence ratio.Equivalence ratio from 0.1 to 0.5 was considered as lean mixture, and for 1.5-1.9 as rich mixture. Equivalence ratio is the ratio of the fuel-to-oxidizer ratio to the stochiometric fuel-to-oxidizer ratio.

$$\phi = \frac{m_{fuel}/m_{OX}}{(m_{fuel}/m_{OX})_{st}}$$

where:
m - mass
st - stechiometric conditions

3.1 Lean mixtures

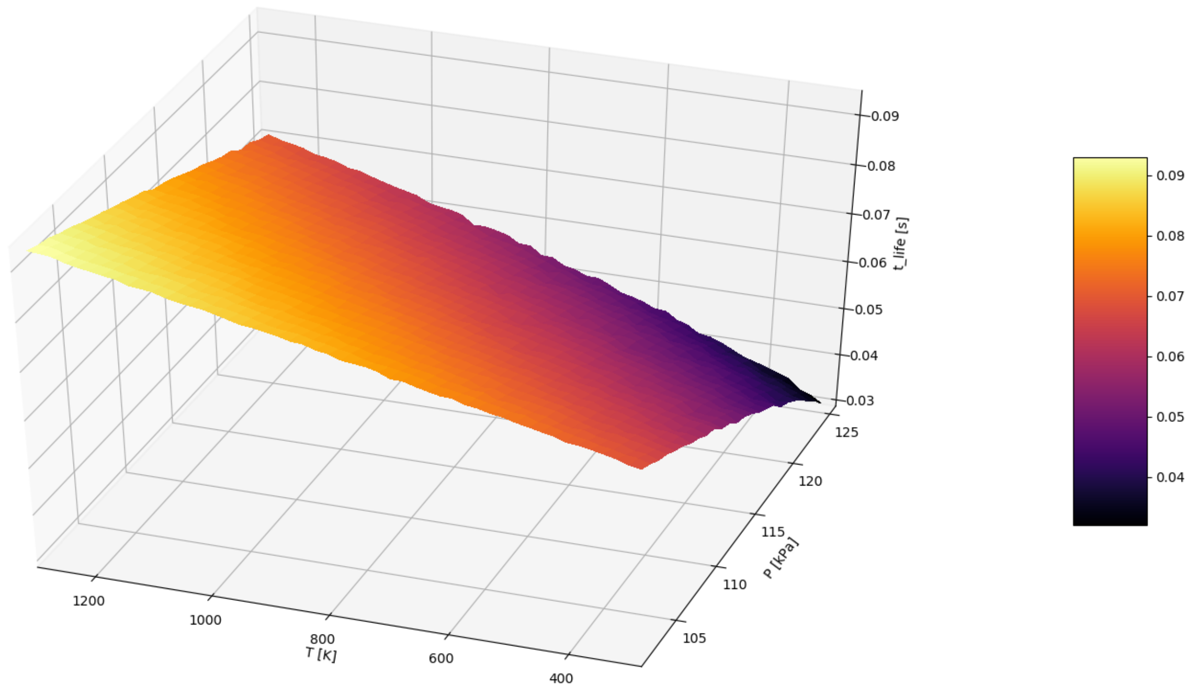

Figure 2.1 The lifespan of hydroxyl radicals with equivalence ratio 0.1

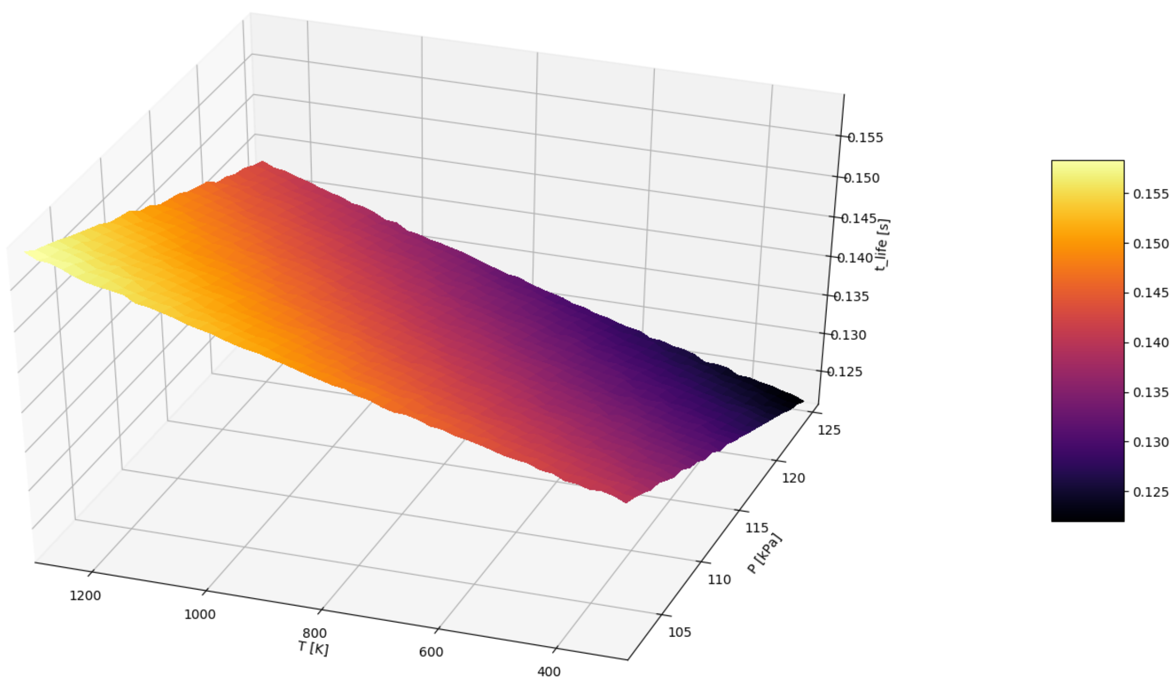

Figure 2.2 The lifespan of hydroxyl radicals with equivalence ratio 0.2

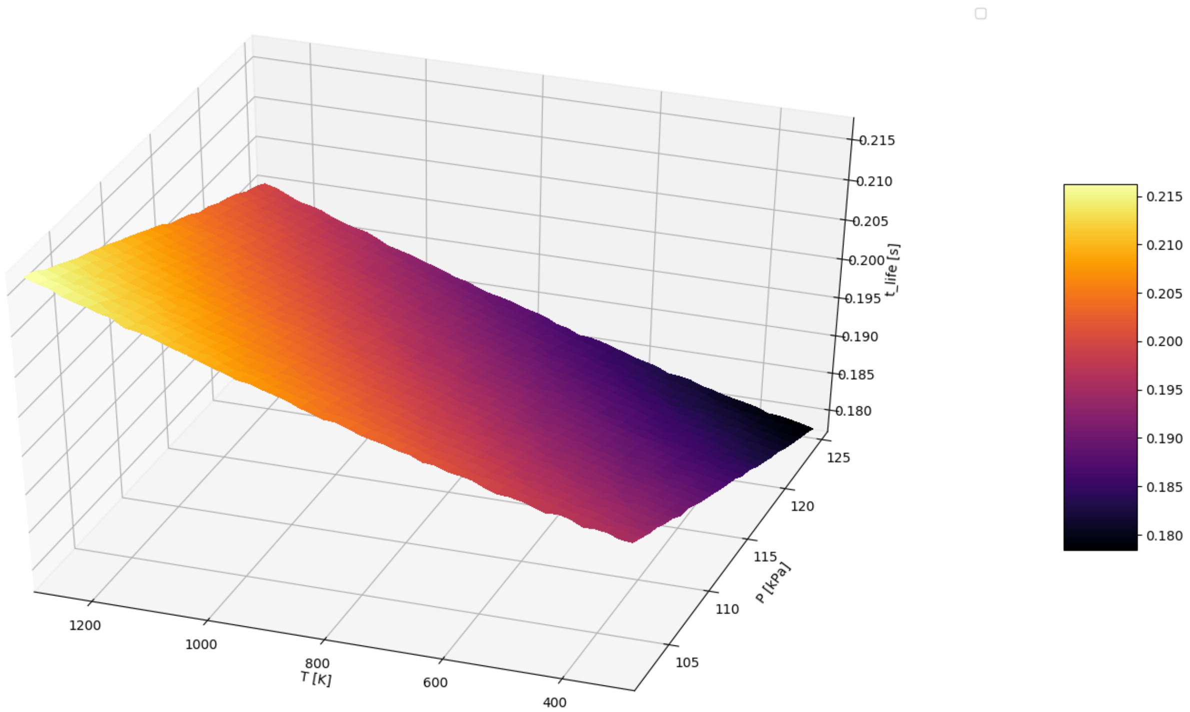

Figure 2.3 The lifespan of hydroxyl radicals with equivalence ratio 0.3

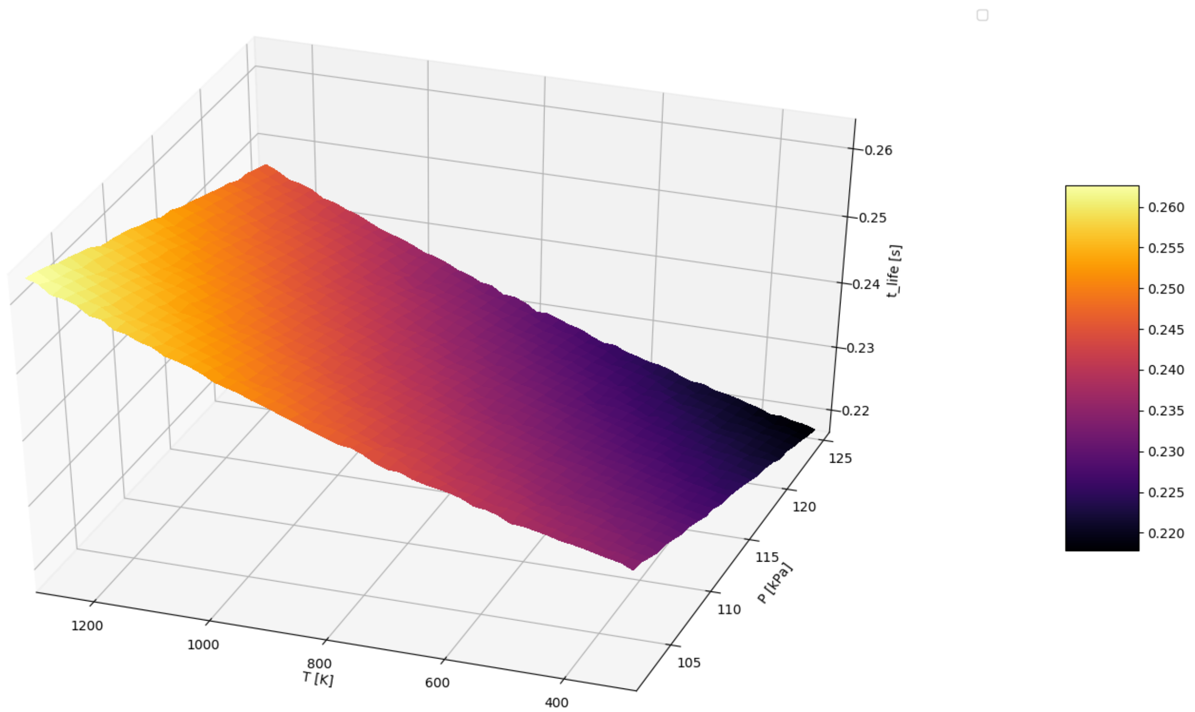

Figure 2.4 The lifespan of hydroxyl radicals with equivalence ratio 0.4

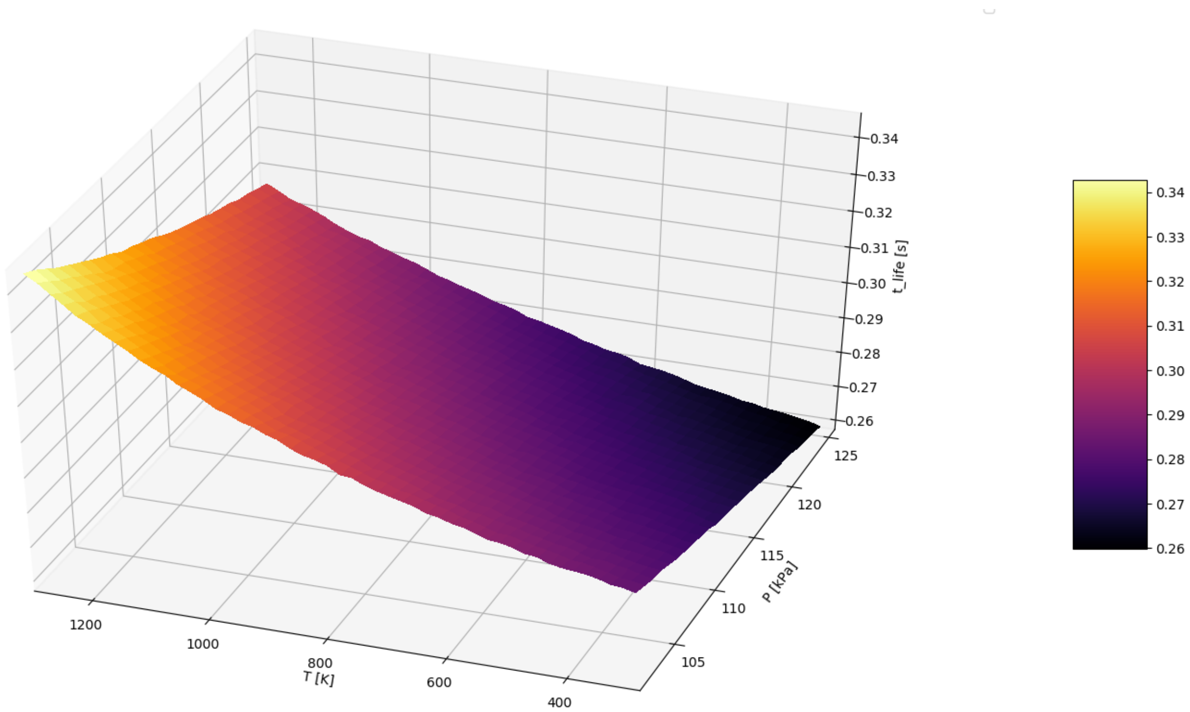

Figure 2.5 The lifespan of hydroxyl radicals with equivalence ratio 0.5

3.2 Rich mixtures

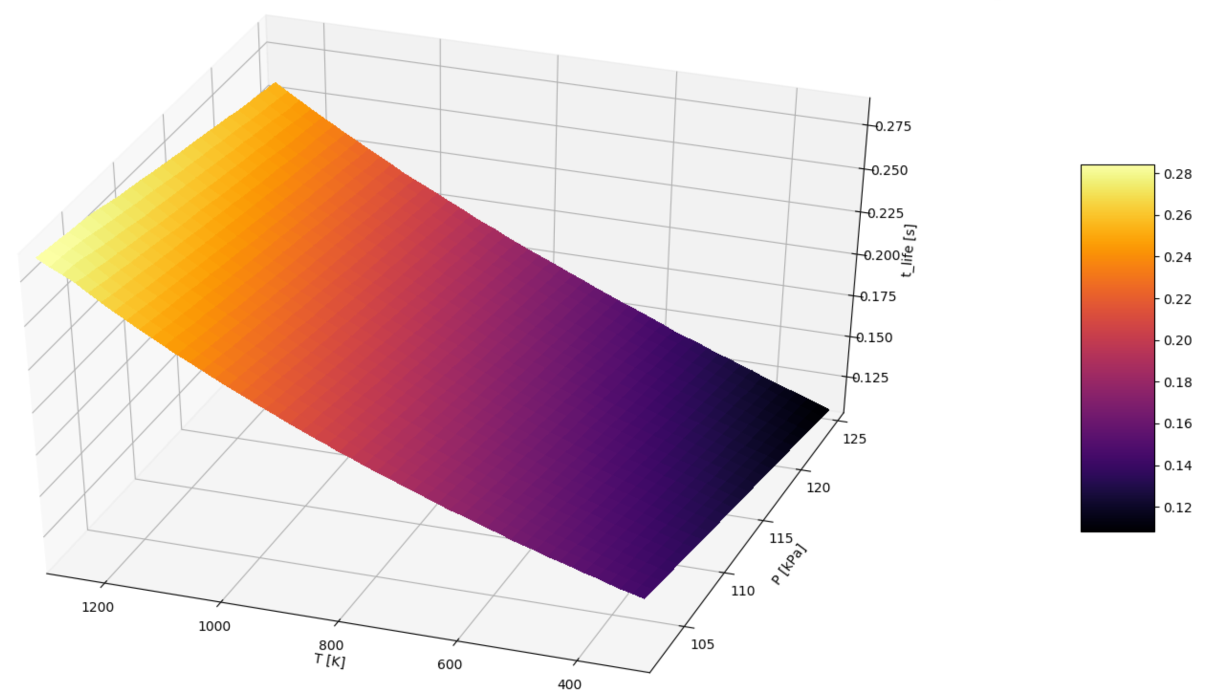

Figure 3.1 The lifespan of hydroxyl radicals with equivalence ratio 1.5

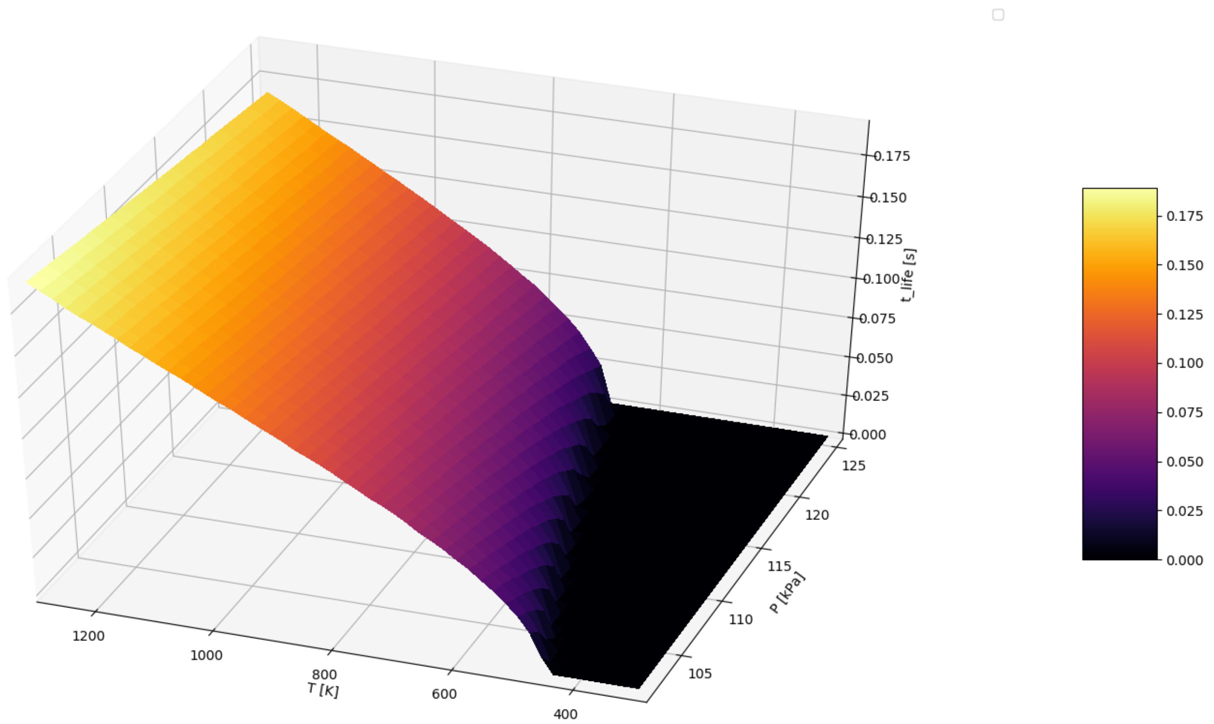

Figure 3.2 The lifespan of hydroxyl radicals with equivalence ratio 1.6

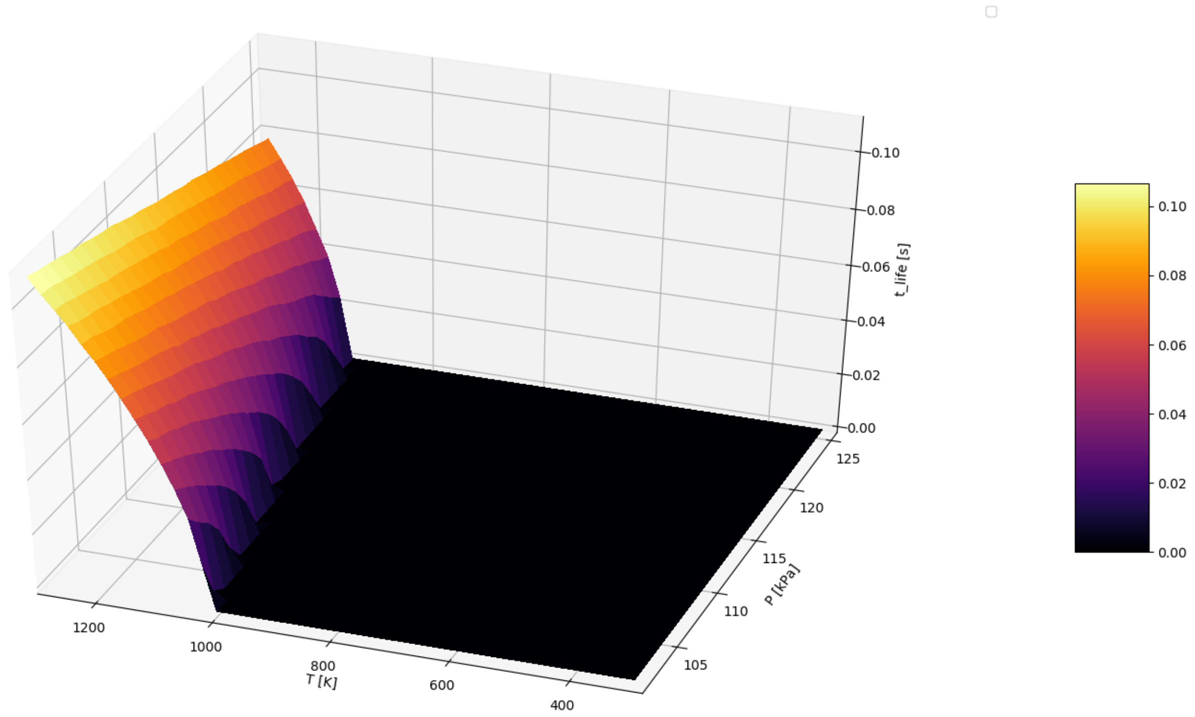

Figure 3.3 The lifespan of hydroxyl radicals with equivalence ratio 1.7

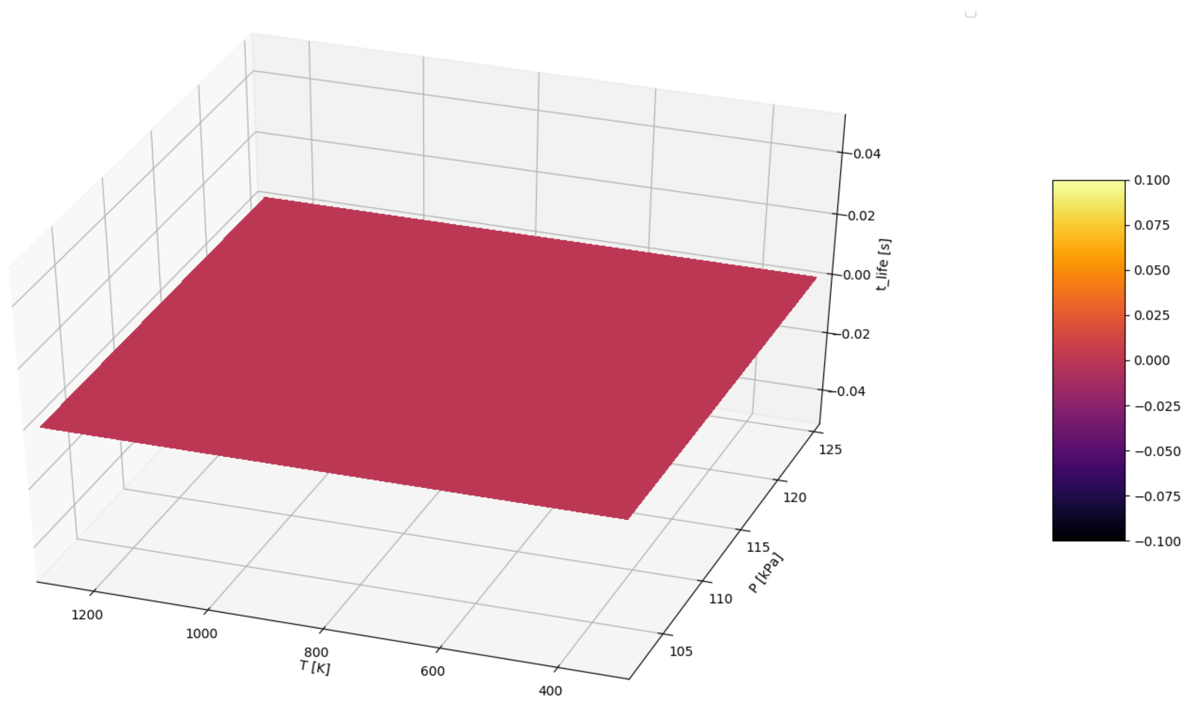

Figure 3.4 The lifespan of hydroxyl radicals with equivalence ratio 1.8

4 Summary

The hydroxyl radicals are very reactive species. This means that they react very fast with other species in the mixture and form new radicals. As the simulations have shown, the lifetime of hydroxyl radicals is very short, from a few up to several milliseconds. It depends on equivalence ratio, the closer we are to stochiometric conditions, the longer lifespan of hydroxyl radical is. Additionally, closer analysis of the graphs reveals that in the higher temperatures, the existence of radicals extends. It is due to the fact that molecules have higher kinetic energy, therefore higher probability of splitting into atoms. Simultaneously, the rise of the pressure lowers the lifespan of hydroxyl radicals.
If we take a look on the results of rich mixtures combustions, we can see that reaction only take place at specific range of temperature and pressure. The reason for that is connected with methane's flammability limits.
To sum up, the calculations gave good results (compared to experimental ones). We have to remember that calculated model was very simple. If the results were to going to be used in design process of any machine, more complex model should be used.

5 Bibliography

[1] Hillier, V.A.W.; Pittuck, F.W. (1966). ”Sub-section 3.2”. Fundamentals of Motor Vehicle Technology. London: Hutchinson Educationa
[2]Kumfer, B.; Skeen, S.; Axelbaum, R. (2008). ”Soot inception limits in laminar diffusion flames with application to oxy-fuel combustion”
[3]W. E. Wilson Jr., R.M. Fristorm Radicals in Flames. APL Technical Digest, July-Auhust 1963
[4]Hayyan M., Hashim M.A., AlNashef I.M. (2016). ”Superoxide Ion: Generation and Chemical Implications”
[5]Model of combustio: Cantera 2.3.0