

MECH 652: Dynamics of Combustion  
PROJECT ASSIGNMENT #2: REACTORS

Name – Swadesh Suman

McGill ID – 261097252

**Part II – Identification of reactions and rate calculation**

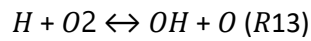
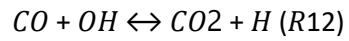
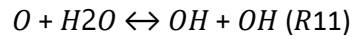
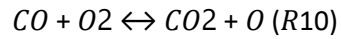
Problem 1: For the different reactions (R1-R6), indicate if they are unimolecular, bimolecular or termolecular

Reaction No	Unimolecular	Bimolecular	Termolecular
R1		R1	
R2		R2	
R3			R3
R4		R4	
R5		R5	
R6		R6	

Problem 2 & 3 : Indicate the reaction type: global, initiation, propagation, branching, termination. Indicate which reaction is pressure dependent.

Reaction No	Reaction Type	Pressure-dependent
R1	Global	Not dependent
R2	Initiation	Dependent
R3	Termination	Dependent
R4	Propagation	Not Dependent
R5	Propagation	Not Dependent
R6	Propagation	Not Dependent

Consider the following elementary reaction system, where both the forward and reverse reactions are important:



Problem 5. Write out the rate equation of OH and O; using the forward and reverse rate ( $k_{i,f}$  and  $k_{i,b}$ ) of the reactions R10 to R13.

$$\begin{aligned} \frac{d[OH]}{dt} = & K_{11,f}[O][H_2O] - K_{11,b}[OH]^2 - K_{12,f}[CO][OH] + K_{12,b}[CO_2][H] + \\ & K_{13,f}[H][O_2] - K_{13,b}[OH][O] \end{aligned}$$

$$\begin{aligned} \frac{d[O]}{dt} = & K_{10,f}[CO][O_2] - K_{10,b}[CO_2][O] - K_{11,f}[O][H_2O] + K_{11,b}[OH]^2 + \\ & K_{13,f}[H][O_2] - K_{13,b}[OH][O] \end{aligned}$$

### Part III – Explosion theory

#### **Adiabatic ignition**

Considering a stoichiometric mixture of iso-octane and air, inside a closed, adiabatic, and constant volume reactor, approximated to a sphere, with the following parameters:  $r = 37\text{mm}$ ,  $T_{in} = 800\text{K}$ , and  $P = 1\text{atm}$ .

Problem 1: Calculate the volume and surface of this reactor

Given,  $r = 0.037\text{ m}$

Using the relation,  $v = \frac{4}{3}\pi r^3$ , the volume of the reactor is  $- 2.121\text{ E-4}$ .

Using the relation,  $s = 4\pi r^2$ , the surface area of the reactor is  $- 1.7203\text{ E-2}$ .

Problem 2. Execute the simulation and calculate the heat release at each time step

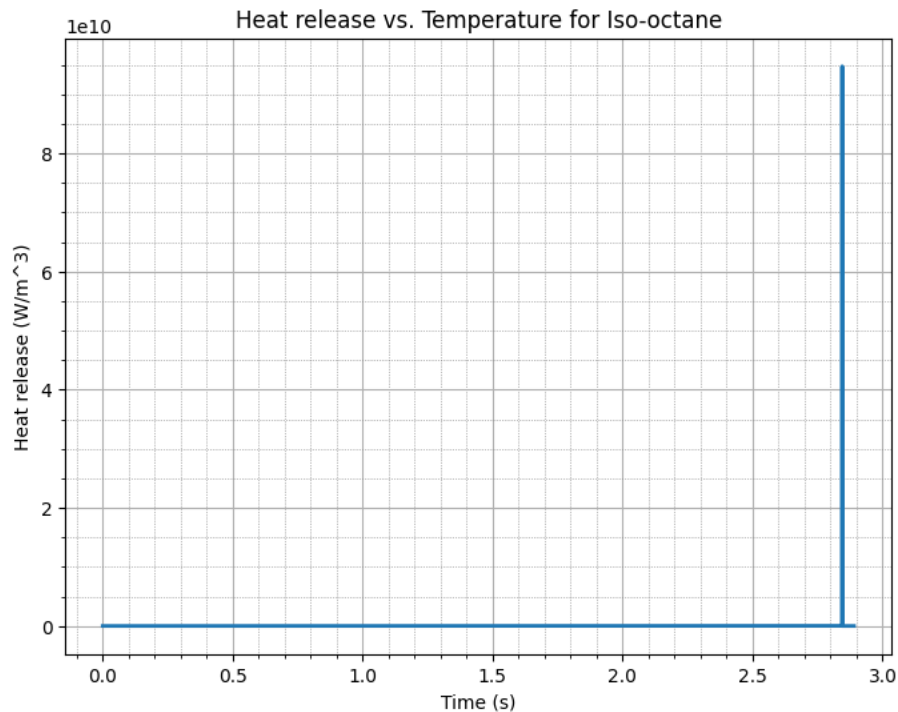


Fig 1 – Heat release vs Temperature ( iso-octane)

Problem 3: Does the mixture ignite? If so, calculate the required time to auto-ignite the mixture.

The initial guess for the ignition delay for iso-octane was set to 5 seconds. The mixture ignited within this time frame. The time required to auto-ignite the mixture was 2.845 seconds.

Problem 4. Plot the heat release of the reactor versus its temperature.

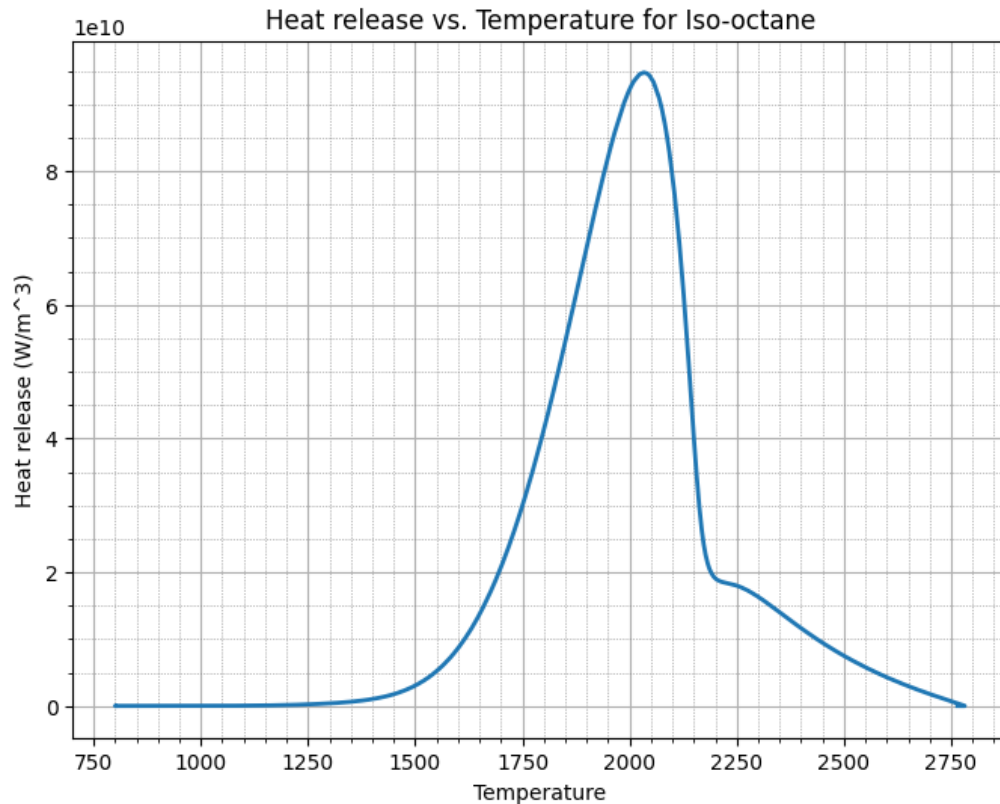


Fig 2 – Heat release vs Temperature ( iso-octane)

Fig 2 shows the heat release vs temperature plot for iso-octane. As shown in the graph, the highest heat release is observed at 2050 K.

Problem 5 : Repeat Q2-4 for a lighter fuel, methane. Comment on the difference on ignition time and heat release.

The initial guess for the ignition delay for methane was set to 200 seconds. The mixture ignited within this time frame. The auto-ignition time of methane is 143.3 seconds, which is much higher than the ignition time for iso-octane. The ignition time for iso-octane is around 2.845 seconds.

Fig 3 on the next page shows the heat release vs temperature plot for methane. The overall heat release for methane is lower as compared to that of iso-octane. The highest heat release rate is observed at lower temperature around 2150 K, whereas for the iso-octane the highest heat release rate is observed around 2050 K.

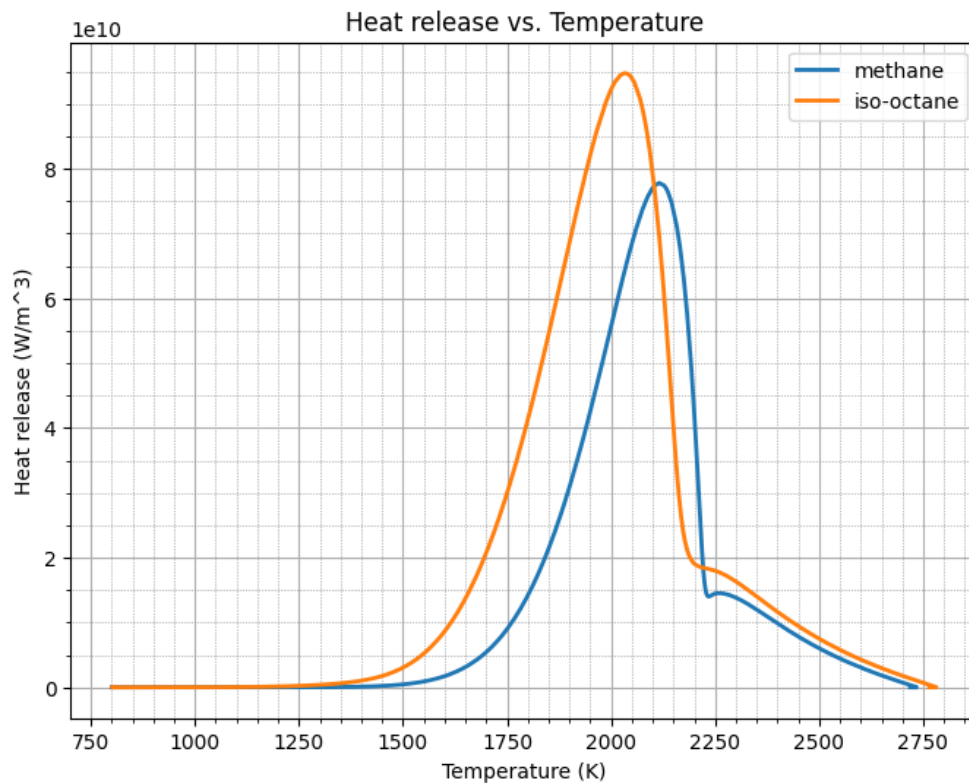


Fig 3 – Heat release vs Temperature ( methane & iso-octane)

### Semenov theory

Using the adiabatic case as a reference, we will introduce theoretical heat loss to the reactor, without executing the simulation.

Problem 6 - Following Cantera's definition of heat loss through a wall, compute the heat loss function, depending on temperature of the adiabatic reactor.

- a) For  $T_{\text{environment}} = 1300\text{K}$  and  $U = 0.1 \text{ MW/m}^2\text{K}$
- b) For  $T_{\text{environment}} = 1100\text{K}$  and  $U = 1.0 \text{ MW/m}^2\text{K}$
- c) For  $T_{\text{environment}} = 1000\text{K}$  and  $U = 2.0 \text{ MW/m}^2\text{K}$

According to the Cantera's definition of heat loss through a wall -  $Q = UA(T_{\text{left}} - T_{\text{right}})$

Where,  $U$ - overall heat coefficient ( $\text{W/m}^2/\text{K}$ ),

$A$  – surface area ( $\text{m}^2$ )

$T_{left}$  – Temperature (K): In our case, this temperature is equal to the temperature of the adiabatic reactor.

$T_{right}$  – Temperature (K): In our case, this temperature is equal to the temperature of the environment.

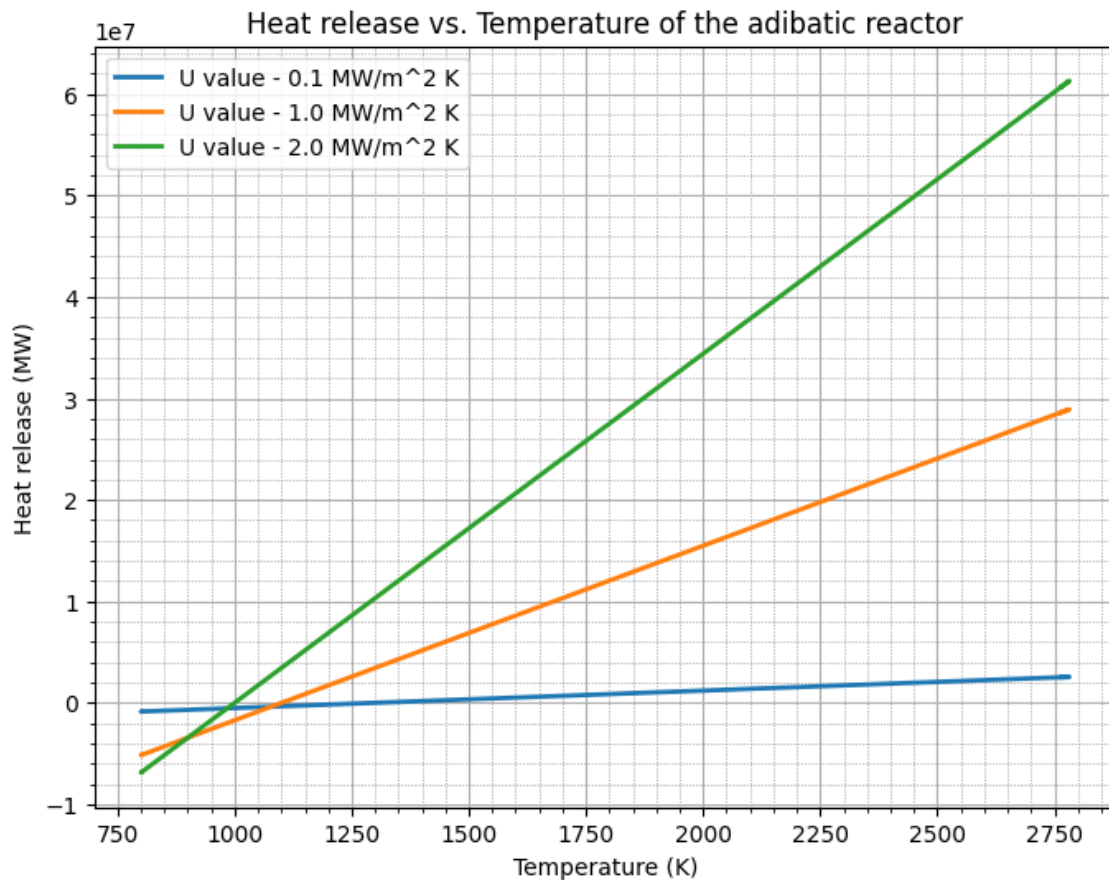


Fig 4 – Heat loss function vs Temperature adiabatic for all three cases

Problem 7: Plot these 3 functions on top of the heat release versus temperature plot from Q4.

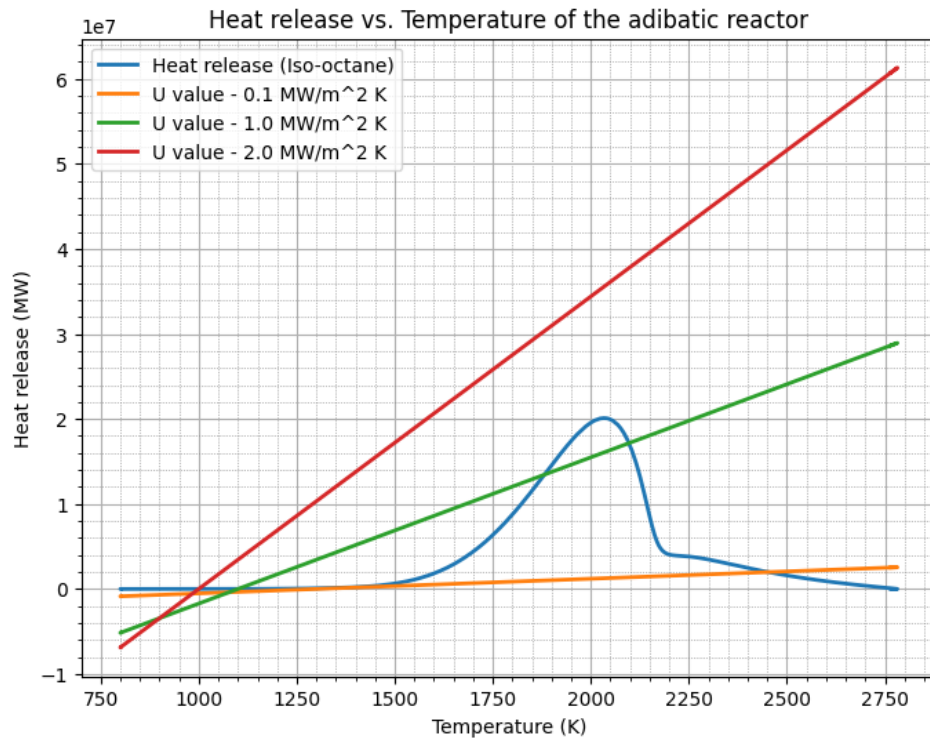


Fig 5 – Heat release vs Temperature adiabatic for Iso-Octane along with heat loss for all three cases

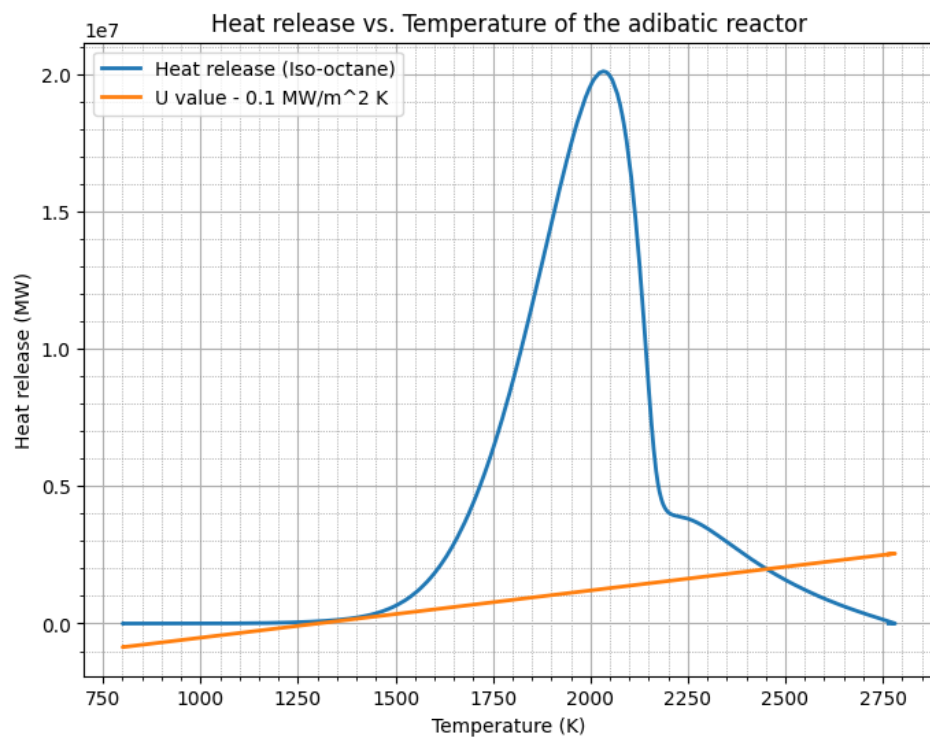


Fig 6 – Heat release vs Temperature adiabatic for Iso-Octane along with heat loss for U – 0.1 MW/m<sup>2</sup>K

Problem 8. Just using the graph, and for each environmental condition, determine if the mixture will ignite.

The mixture will ignite for the first case, i.e.,  $U = 0.1 \text{ MW/m}^2\text{K}$ . The heat loss function is tangent to heat release curve for iso-octane, and hence it will form the stable point at its intersection with the heat release curve.

For other two cases, the mixture will not ignite.

Problem 9 & 10. Confirm your theory by computing a reactor with the same heat loss functions than for Q6. Consider emissivity  $\epsilon$  and the heat flux function  $q''(t)$  to be 0. If it does ignite, calculate the required time to auto-ignite the mixture and compare the value to the adiabatic case. What can you conclude?

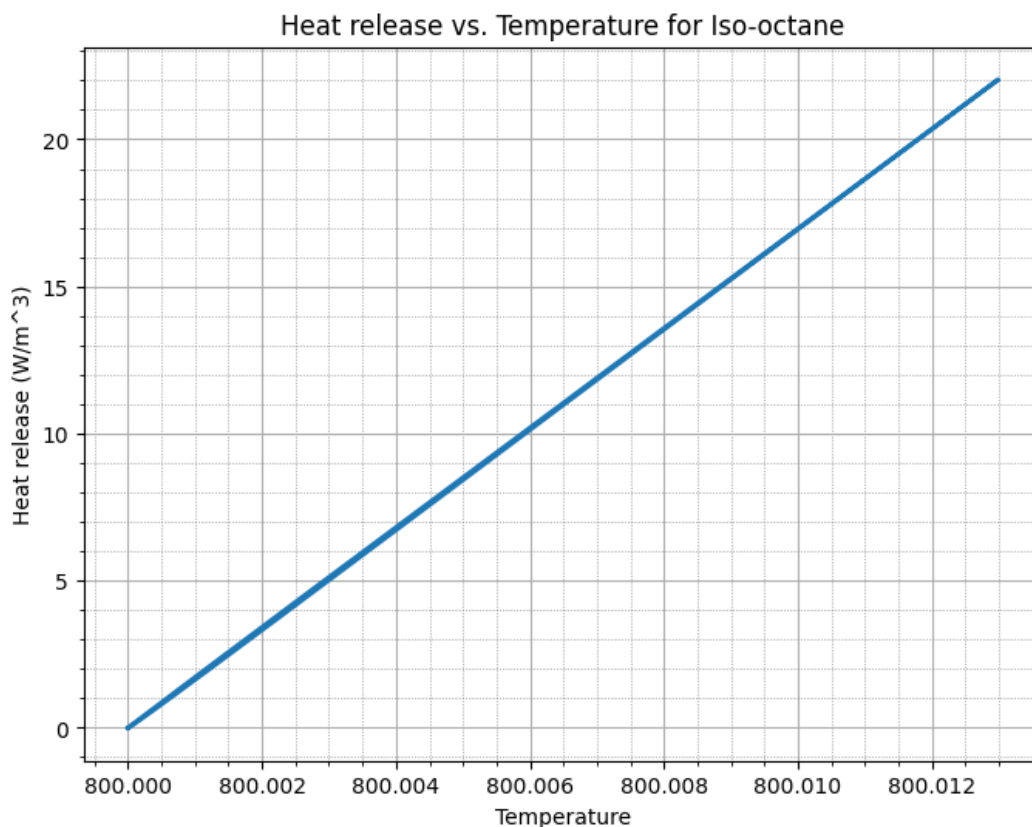


Fig 7 – Heat release vs Temperature adiabatic (Iso-Octane) for  $U = 0.1 \text{ MW/m}^2\text{K}$

The mixture is not getting ignited for any of three cases of  $U$ . Ideally, the mixture should have ignited for the first case of  $U = 0.1 \text{ MW/m}^2\text{K}$ . But there is no ignition even with assuming higher ignition delay time like 1000 s.



## Hydrogen S-curve

Using again an adiabatic reactor, we will determine the explosivity of hydrogen-air depending on pressure and temperature. By iterating on pressure from 1/1000atm to 10,000atm in step of 10n , vary the inlet temperature in step of 10K from 650K to 950K until you reach ignition. For this case, use an estimated ignition delay of 10s.

Problem 11. Compute the ignition temperature (meaning the initial temperature required to ignite the mixture at this pressure) for each pressure step. Plot these results on a semi-log graph. Comment your results. What reactions are at play?

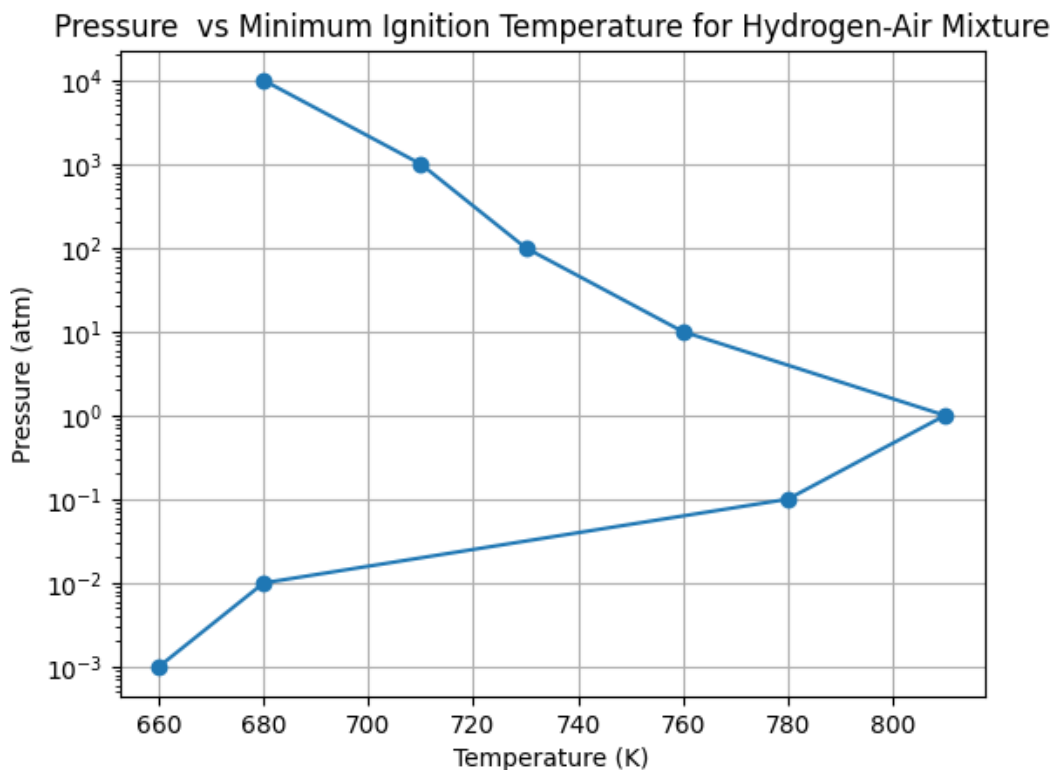


Fig 8 – Pressure vs Ignition Temperature adiabatic (Hydrogen-Air Mixture)

- In the above graph, it is seen that ignition temperature varies with pressure for the hydrogen-air mixture.
- Generally, as pressure increases, the ignition temperature also increases, indicating that higher pressures require higher temperatures for ignition.
- After a certain limit of pressure (1 atm in this case), the ignition temperature starts decreasing.
- The reactions at play involve the combustion of hydrogen ( $H_2$ ) with oxygen ( $O_2$ ) to form water vapor ( $H_2O$ ). These reactions are highly temperature and pressure-dependent and follow complex chemical kinetics.

Problem 12. Why is the S-curve not fully described at low pressure?

For the low-pressure, the difference between the ignition limit and extinction limit is reduced significantly, hence it is difficult to fully define S-curve at low pressure.

Moreover, the low-pressure regime is often dominated by slow reactions, and the chemistry of hydrogen combustion may not fully activate until higher pressures are reached. This means that at very low pressures, the ignition delay behavior may not exhibit the characteristic S-curve shape.

**Part IV –Constant pressure ignition**

In the case of a constant pressure reactor, the pressure is held constant while the volume is varying. This is an example of the combustion chamber of a gas turbine. Using a constant pressure reactor:

Problem 1. For  $P = 1\text{atm}$ , calculate the autoignition delay for a stoichiometric mixture of iso-octane and air for a range of temperature from 500K to 1600K, in steps of 50K. Plot the autoignition delay vs T on a semilog plot.

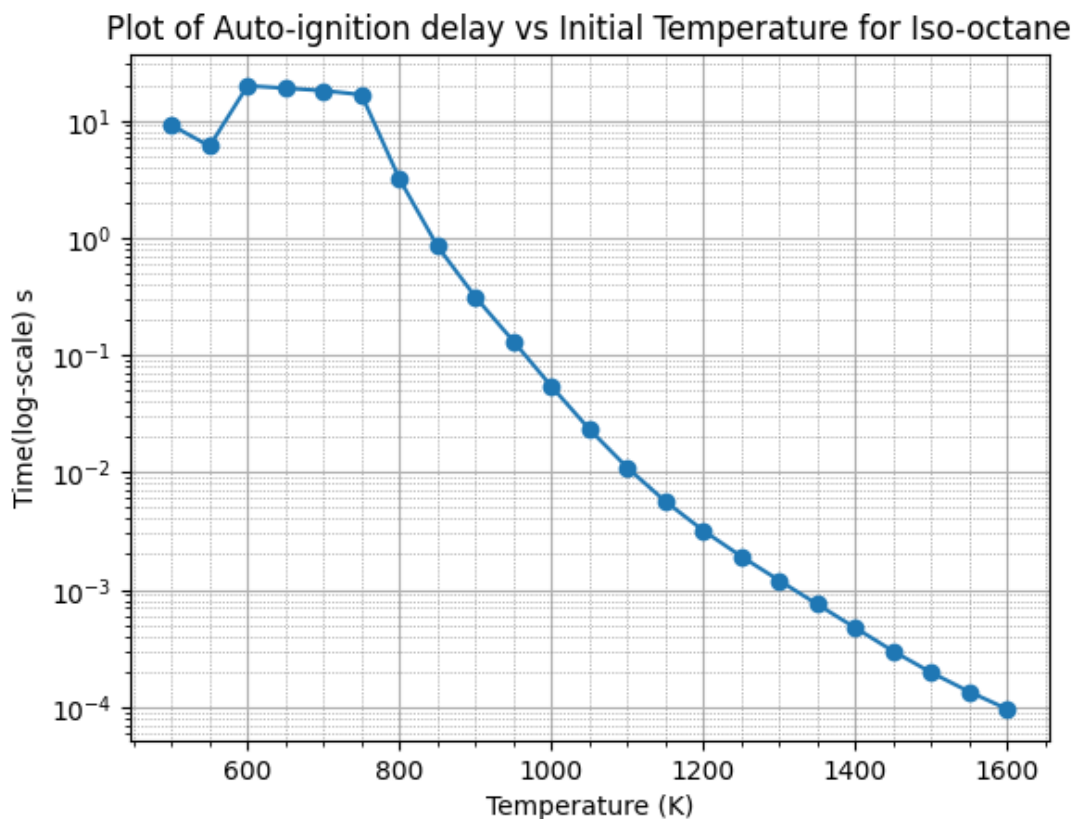


Fig 9 – Auto-Ignition delay time vs Ignition Temperature (Iso-Octane)

Problem 2. Repeat the question but using methane instead.

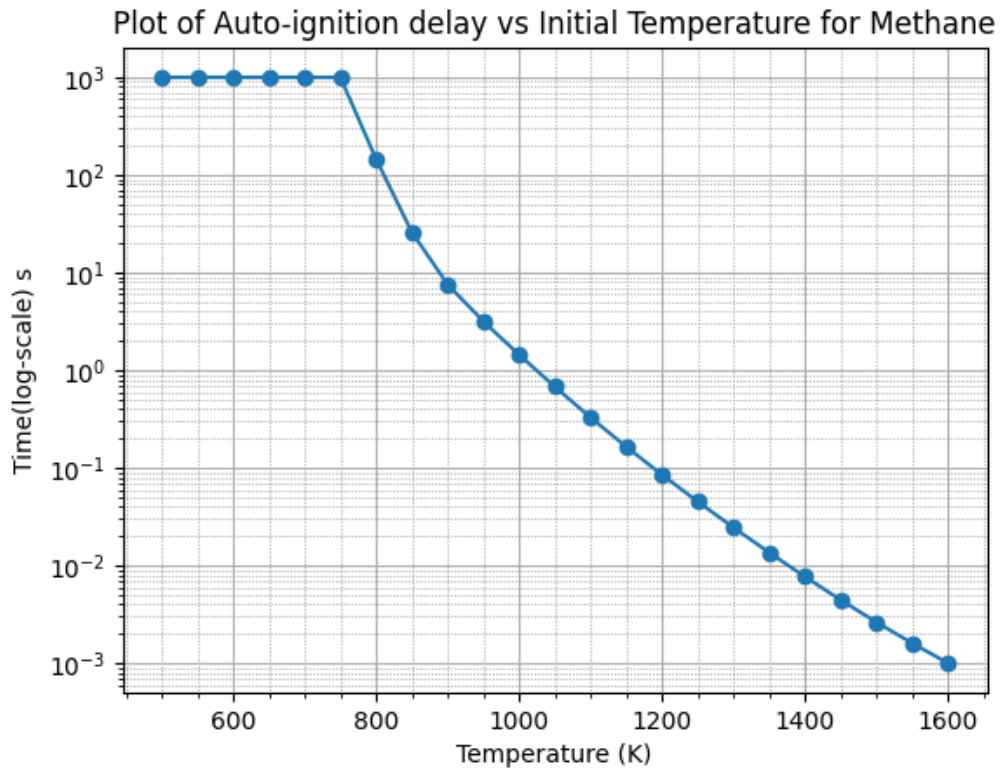


Fig 10 – Auto-Ignition delay time vs Ignition Temperature (Methane)

Problem 3. Comment on the differences of the results.

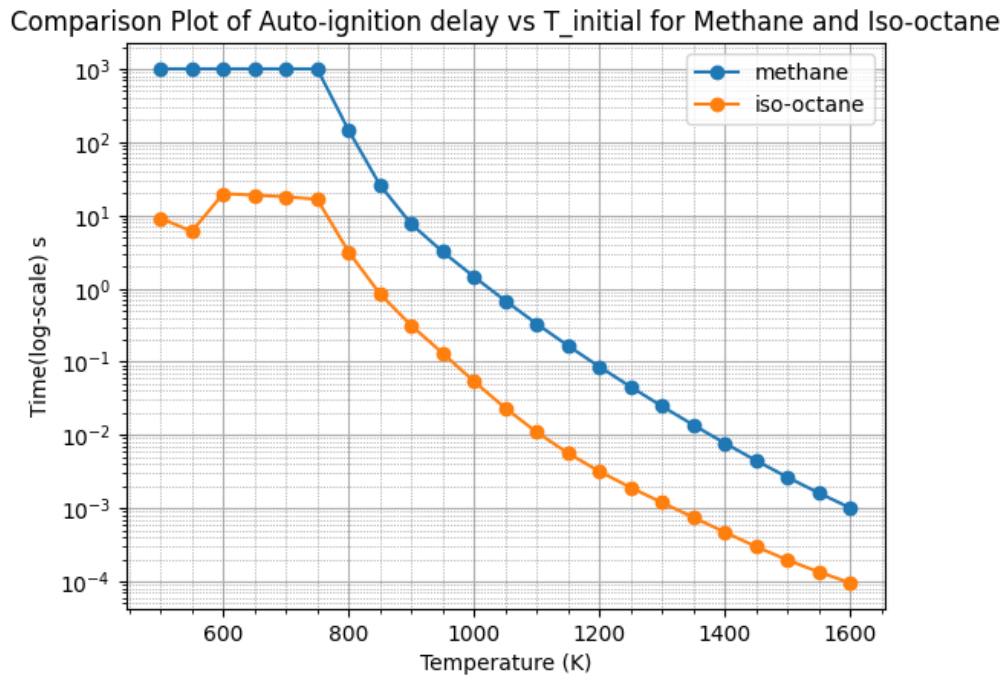


Fig 11 – Auto-Ignition delay time vs Ignition Temperature (Methane and Iso-Octane)

- The auto-ignition time for methane is higher than iso-octane at all initial temperatures.
- Methane does not ignite at lower initial temperatures even with higher assumption of ignition delay times. The ignition for methane starts around 766 K.
- Iso-Octane ignites at all initial temperature. The Iso-octane being a complex compound has more free radicals which leads to higher number of reaction pathways compared to methane, and hence the lower auto-ignition delay time.

Problem 4. What would an increase of pressure change to the ignition delay? Explain.

An increase in pressure typically decreases the ignition delay of a combustible mixture. This is primarily due to-

- Increased number of molecular collisions between reactant molecules (fuel and oxidizer) which probability of effective collisions leading to chemical reactions.
- An increase in pressure raises the initial temperature of the mixture (according to Ideal gas Law keeping the volume constant), making it more likely for autoignition to occur, especially at lower temperatures.

Problem 5 : For  $P = 1\text{atm}$ , using 'seiser.yaml', calculate the autoignition delay for a stoichiometric mixture of nheptane and air for a range of temperature from 500K to 1600K. Note n-heptane is affected by low temperature chemistry, so you must adapt the T step to capture the negative coefficient region correctly.

- a) For each initial temperature, plot the temperature profile versus time. Comment on the evolution of the profiles with T.

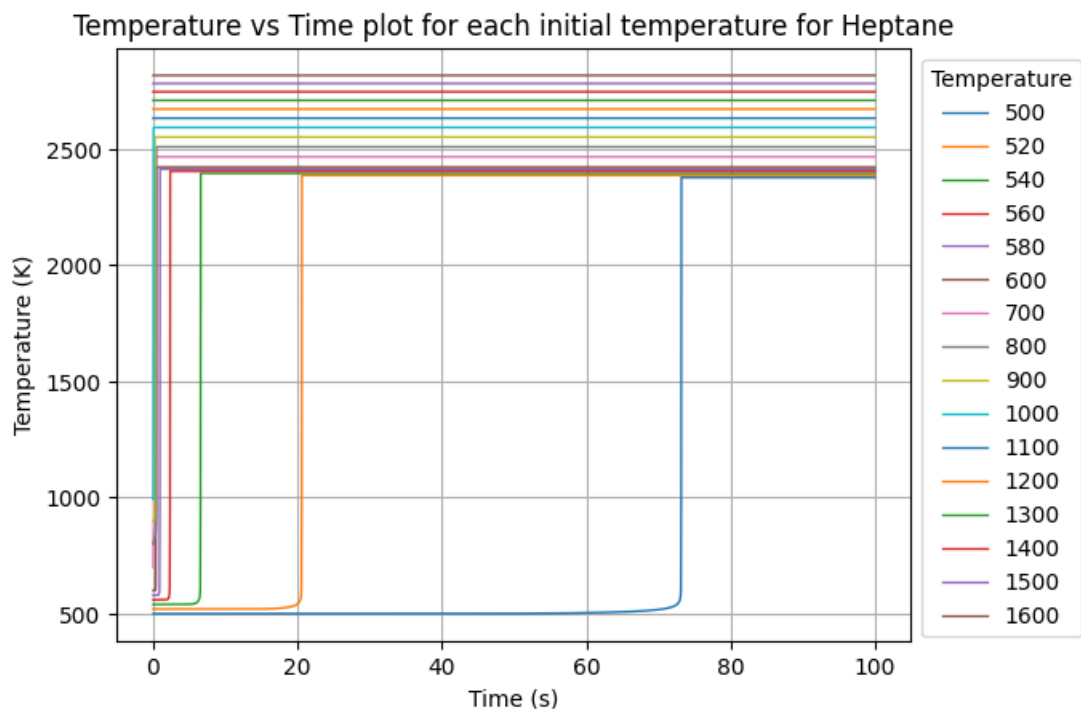


Fig 12 – Temperature profile evaluation with each initial temperature

For the proper visualization purpose, the variation of initial temperature has been a little bit modified. Each curve in fig 12 represents the temperature evolution over time at a specific initial temperature in K.

- At lower initial temperatures, the temperature rises gradually, reflecting slower reactions. The ignition delay, the time it takes for the temperature to sharply increase, is longer at lower initial temperatures.
- As the initial temperature increases, the temperature rise becomes more rapid, indicating faster reactions. The ignition delay decreases with increasing initial temperature.
- Eventually, at a certain threshold temperature, the mixture autoignites, resulting in a sharp increase in temperature. This threshold temperature represents the autoignition temperature, and it decreases as the initial temperature increases.

- b) Plot the autoignition delay vs  $1000/T$  on a semilog graph. Comment on the negative-temperature coefficient region.

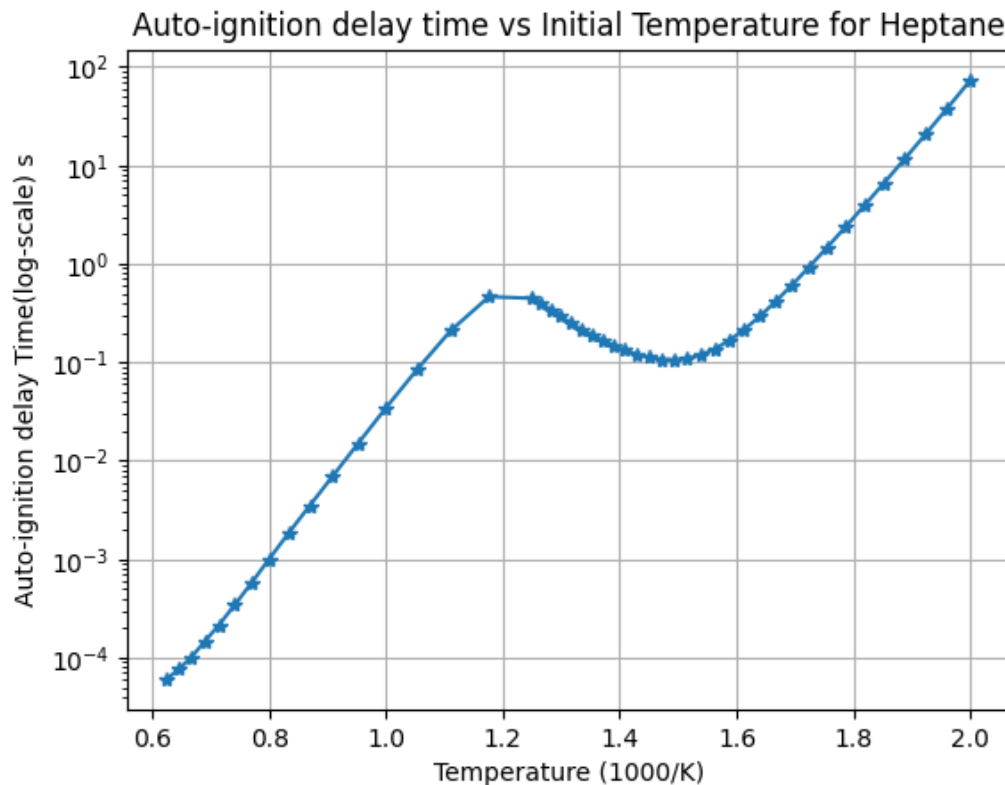


Fig 13 – Auto Ignition delay time vs Initial temperature for Heptane

In the fig 13 of autoignition delay time plot vs.  $1000/\text{Temperature}$  for heptane-air mixture, the presence of a negative temperature coefficient (NTC) region can be observed. It is characterized by a non-monotonic behavior of the autoignition delay with respect to temperature.

In the NTC region of the graph, the autoignition delay initially increases as the temperature decreases and then decreases again as the temperature continues to decrease. This behavior is contrary to what one might expect, as reactions generally speed up with increasing temperature.

This is because of the Low-Temperature Kinetics. At lower temperatures, the reaction kinetics for some key species are relatively slow. This includes reactions involving fuel oxidation, radical formation, and chain branching. As a result, the overall combustion process proceeds slowly, leading to a longer autoignition delay.

## **Part V – Perfectly stirred reactor**

In industry, the design of a new combustor often starts with first estimations obtained from 0D reactors such as perfectly stirred reactors (PSR). The preliminary goal is to find the best configuration to reduce pollutant formation (e.g. NO<sub>x</sub>, CO, unburned hydrocarbons (UHC), etc.). In this homework assignment, we will look at the effect of air admission in the combustor on the pollutant emissions. We will consider an aero-derivative gas turbine with an efficiency of 42% and a power output of 120 MW. The total air flow rate, fixed by the compressor at 240 kg/s, enters the 0.40 m<sup>3</sup> combustor at 30 atm at a temperature of 800K.

Problem 1: From the information given above, calculate the required mass flow rate of iso-octane at full load for the above conditions, as well as the overall equivalence ratio, assuming a heating value of 45 MJ/kg.

To calculate the required mass flow rate of iso-octane and the overall equivalence ratio for the given conditions, we'll need to follow these steps:

Step 1: Calculate the power input to the combustor.

Step 2: Calculate the fuel mass flow rate.

Step 3: Calculate the overall equivalence ratio ( $\Phi$ ).

Step 1: Calculate the power input to the combustor

The power output of the gas turbine is 120 MW, and the efficiency is 42%. The power input to the combustor can be calculated as follows:

$$\text{Power Input} = \text{Power Output} / \text{Efficiency}$$

$$\text{Power Input} = 120 \text{ MW} / 0.42$$

$$\text{Power Input} = 285.714 \text{ MW}$$

Step 2: Calculate the fuel mass flow rate.

The heating value of iso-octane is given as 45 MJ/kg. We can calculate the fuel mass flow rate using the following formula:

$$\text{Fuel Mass Flow Rate} = \text{Power Input} / \text{Heating Value}$$

$$\text{Fuel Mass Flow Rate} = (285.71 \text{ MW}) / (45 \text{ MJ/kg})$$

$$\text{Fuel Mass Flow Rate} = 6.349 \text{ kg/s}$$

Step 3: Calculate the overall equivalence ratio ( $\Phi$ ).

For iso-octane, the stoichiometric air-fuel ratio is typically around 15.022 (by mass) for complete combustion.

The total air flow rate is given as 240 kg/s. To calculate the AFR, divide the air mass flow rate by the fuel mass flow rate:

$$\text{AFR} = \text{Air Mass Flow Rate} / \text{Fuel Mass Flow Rate}$$

$$\text{AFR} = 240 \text{ kg/s} / 6.346 \text{ kg/s}$$

$$\text{AFR} = 37.801$$

The overall equivalence ratio ( $\Phi$ ) is a measure of how rich or lean the mixture is compared to stoichiometric conditions. It is defined as:

$$\Phi = (\text{Stoichiometric AFR}) / (\text{Actual AFR})$$

$$\Phi = 15.022 / \text{AFR}$$

$$\Phi = 15.022 / 37.801$$

$$\Phi = 0.397$$

So, the overall equivalence ratio for these conditions is 0.397.

Problem 2: For these conditions (composition, temperature, and pressure), calculate the equilibrium flame temperature, and mole fractions of CO, NO, and CO<sub>2</sub>.

- The equilibrium flame temperature for these conditions is 1718.5 K.
- The mole fraction of CO for these conditions is 2.273 E-06.
- The mole fraction of NO for these conditions is 2.356 E-03.
- The mole fraction of CO<sub>2</sub> for these conditions is 5.187 E-02.

Problem 3: Assume the combustor can be simulated using a single PSR with the above cited volume, calculate the concentration of CO, NO, and CO<sub>2</sub>.

- The mole fraction of CO for these conditions using PSR is 8.188 E-06.
- The mole fraction of NO for these conditions using PSR is 4.537 E-05.
- The mole fraction of CO<sub>2</sub> for these conditions using PSR is 5.185 E-02.

Problem 4. What is the residence time for these conditions?

The residence time for these conditions is around 1.37E-04 s.

Problem 5: How do the PSR concentration values for CO, and NO compare with the equilibrium values. Explain the differences between the concentration for these 2 calculations.

1. CO Concentration:

Equilibrium Value: 2.273 E-06

PSR Value: 8.187 E-06

Difference: The PSR simulation predicts a higher concentration of CO compared to the equilibrium value. The CO concentration corresponds to unburnt hydrocarbons. The equilibrium concentration for CO is calculated at a specific temperature and pressure where chemical reactions have reached thermodynamic equilibrium, but PSR being a dynamic reactor, combustion reaction occur at different rates. This might be the reason for different CO concentration.

2. NO Concentration:

Equilibrium Value: 2.356 E-03

PSR Value: 4.545 E-05

Difference: The PSR simulation predicts a much lower concentration of NO compared to the equilibrium value. NO concentration being temperature dependent, as the temperature values for PSR and equilibrium values are different, the NO concentration will also be different. In PSR, the local temperature can also be higher, which can result in higher NO.

Problem 6. Explain the difference between the PSR temperature and the equilibrium temperature calculation.

Equilibrium Value: 1718.5 K.

PSR Value: 1723.9 K

Difference: The PSR simulation predicts a little higher temperature value compared to the equilibrium temperature value. The PSR temperature represents the actual temperature within the reactor during the combustion process, whereas the equilibrium temperature is the ideal temperature at which the combustion process reaches thermodynamic equilibrium, and it does not take into account the transient nature of combustion process. Hence the temperature value can be different.

Bonus question: write a script to prove your argumentation for item 5 and 6.

The complete code can be written in the following steps 1 to 19 –

Step 1: Import necessary libraries such as Cantera and NumPy through the following commands:

- Import Cantera as ct
- Import NumPy as np

Step 2: Define a list of species to find composition at equilibrium and list to store variable for PSR:

- species\_list = ["CO", "NO", "CO2"]
- Initialize data\_psr = [4]



Step 3: Create a Cantera gas object:

- Initialize gas = ct.Solution('Jerzembek.yaml')

Step 4: Define the initial conditions:

- Set T\_initial = 800.0 K
- Set P\_initial = 30 atm

Step 5: Set the initial temperature and pressure for the gas object:

- Use gas.TP = T\_initial, P\_initial \* 101325
- Set the equivalence ratio using gas.set\_equivalence\_ratio

Step 6: Create a reservoir for the reactant inlet:

- Initialize inlet = ct.Reservoir(gas)
- Equilibrate the gas composition using gas.equilibrate('HP') for just the reservoir

Step 7: Create an ideal gas reactor (combustor):

- Initialize combustor = ct.IdealGasReactor(gas)
- Define the volume of the combustor (Combustor\_volume)

Step 8: Create a reservoir for the exhaust:

- Initialize exhaust = ct.Reservoir(gas)

Step 9: Define a function to calculate mass flow rate:

- mdot(t) returns combustor.mass / residence\_time

Step 10: Create a MassFlowController for the reactant inlet:

- Initialize inlet\_mfc = ct.MassFlowController(inlet, combustor, mdot=mdot)

Step 11: Create a PressureController for the exhaust:

- Initialize outlet\_mfc = ct.PressureController(combustor, exhaust, primary=inlet\_mfc, K=0.01)

Step 12: Initialize the simulation network:

- Initialize sim = ct.ReactorNet([combustor])

Step 13: Initialize variables for tracking temperature difference and residence time:

- Set T\_difference = 100
- Set residence\_time = 1
- Set T\_initial\_combustor = 800

Step 14: Run a loop over decreasing residence times until the reactor is extinguished:

- While  $T\_difference > 1e-4$ :
  - Reset the integrator: `sim.initial_time = 0.0`
  - Advance the simulation to a steady state: `sim.advance_to_steady_state()`
  - Append the current state to the SolutionArray states with extra parameter 'tres'
  - Update  $T\_difference$  based on the new temperature
  - Update  $T\_initial\_combustor$  with the current temperature
  - Decrease the residence\_time for the next iteration

Step 15: For each species in species\_list:

- Calculate mole fractions in the combustor: `mole_fractions = combustor.thermo[sp].X`
- Depending on the species, update `data_psr` accordingly

Step 16: Initialize variables for tracking species composition at equilibrium:

- Set `species_list_const_Pin_Tin` as an array of zeros
- Initialize `data_equilibrium = [4]`

Step 17: Set initial conditions for gas to compute equilibrium:

- Use `gas.TP = T_initial, P_initial * 101325`
- Set the equivalence ratio using `gas.set_equivalence_ratio`
- Equilibrate the gas composition using `gas.equilibrate('HP')`

Step 18: Calculate adiabatic flame temperature and update `data_equilibrium` accordingly.

Step 19: Print the results for both PSR and equilibrium composition.

To increase the power output of the combustor, the mass flow rate of fuel is increased, as the flow rate of air is generally a fixed parameter tied of the design of the turbine. Thus, an increase of power leads to an increase of equivalence ratio, and a reduction of the residence time

Problem 7. Looping through different power output, from 100MW to 350MW, in steps of 50MW.

- Recalculate the mass flow rate of fuel, equivalence ratio and residence time.
- Repeating the PSR simulation, plot the molar fraction of CO<sub>2</sub>, CO, and NO, as well as the temperature, with residence time. Explain the behaviors.

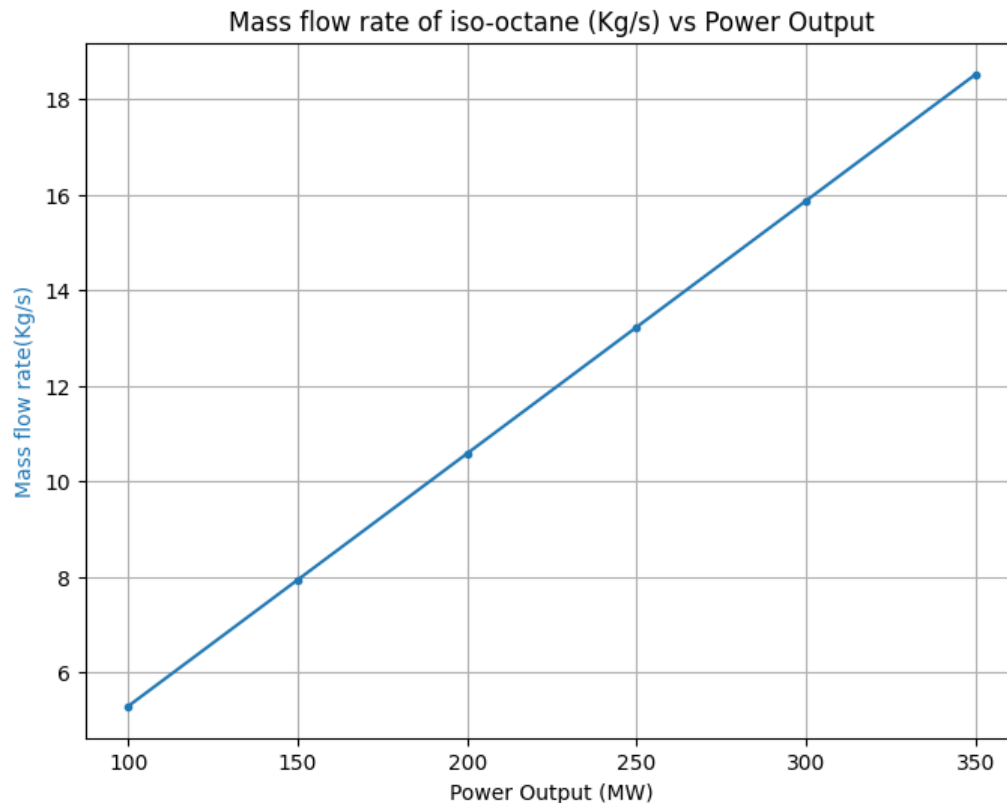


Fig 14 – Mass Flow rate vs Power Output

As the power output requirement increases from 100 MW to 350 MW, the mass flow rate of fuel required also increases from 5.291 to 18.519 Kg/s as shown in the fig 14. Increased mass flow rate of fuel increases the power output.

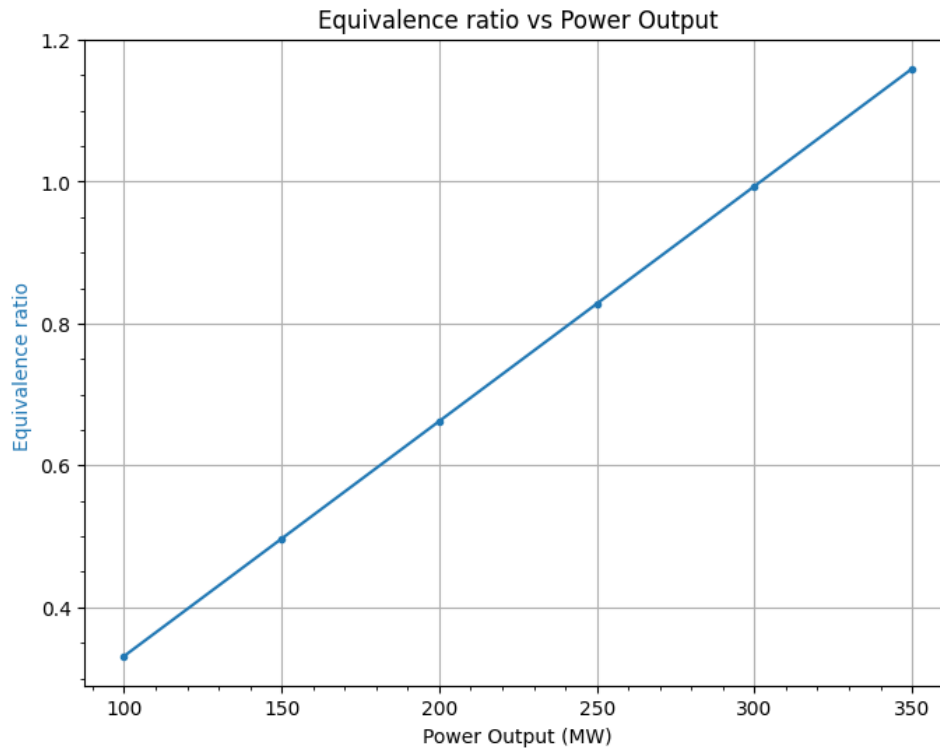


Fig 15 – Equivalence ratio vs Power Output

As the power output requirement increases from 100 MW to 350 MW, the overall equivalence ratio also increases from 0.331 to 1.159 as shown in the fig 15. Increasing the mass flow rate of fuel, decreases the actual air fuel ratio bringing it closer to stoichiometric air fuel ratio.

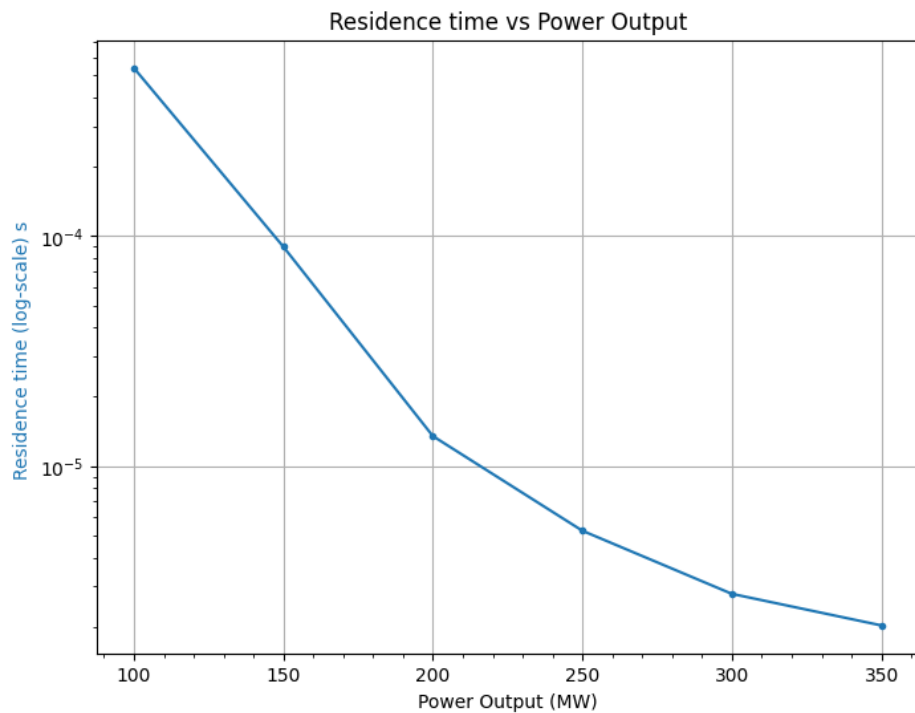


Fig 16 – Residence time (s) vs Power Output

As the power output requirement increases from 100 MW to 350 MW, the residence time decreases from 4.638 E-04 to 1.742 E-06 as shown in the fig 16. To increase the power output, more fuel need to be passed in the reactor, and hence the flow rate increases which leads in shorter residence time.

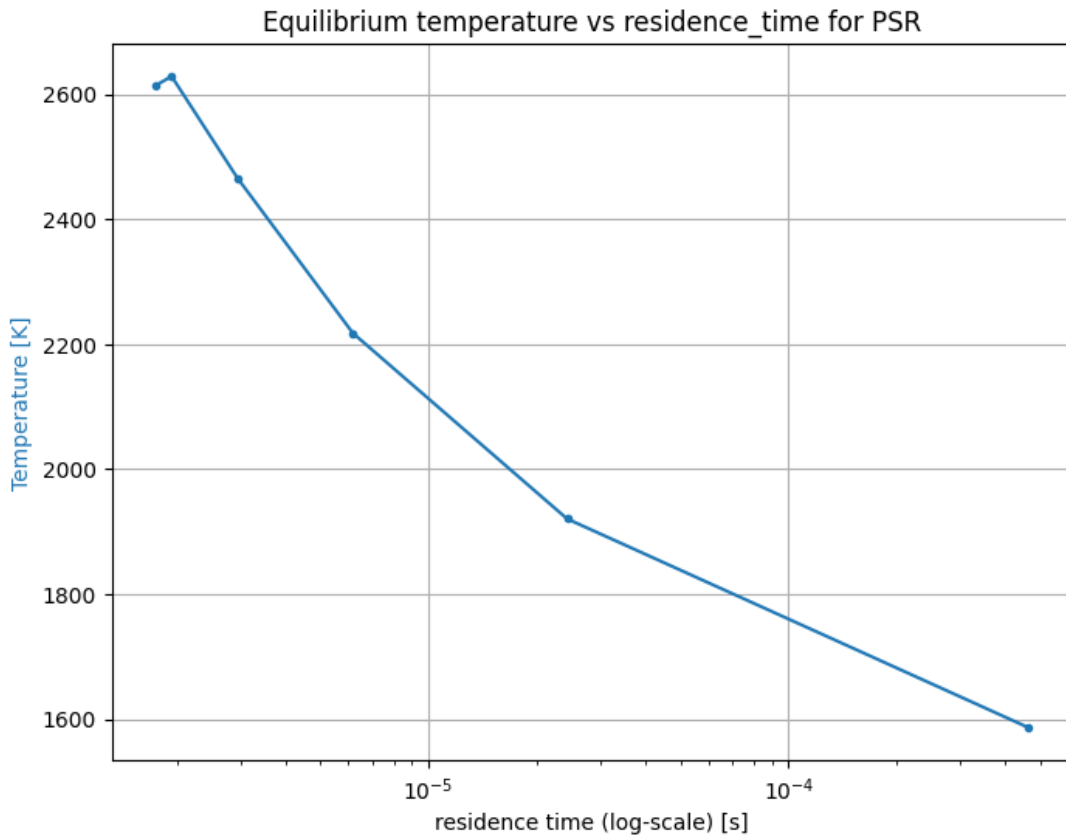


Fig 17 – Equilibrium temperature for PSR (s) vs Residence time

- Fig 17 shows the variation of Equilibrium temperature for PSR by residence time. As the residence time decreases with increasing power output, the overall equilibrium temperature increases. More fuel corresponds in shorter residence time, and higher heating value in the reactor and hence the high temperatures.
- There is a slight drop of the equilibrium temperature at the power output corresponding to 350 MW, where the equivalence ratio value is around 1.15. Since, this phi value corresponds to fuel rich value, the highest temperatures decreases.

Fig 18 on the next page, shows the variation of mole fraction of CO, NO, CO<sub>2</sub> by residence time. As the residence time decreases with increasing power output, the mole fraction of CO, NO, CO<sub>2</sub> increases.

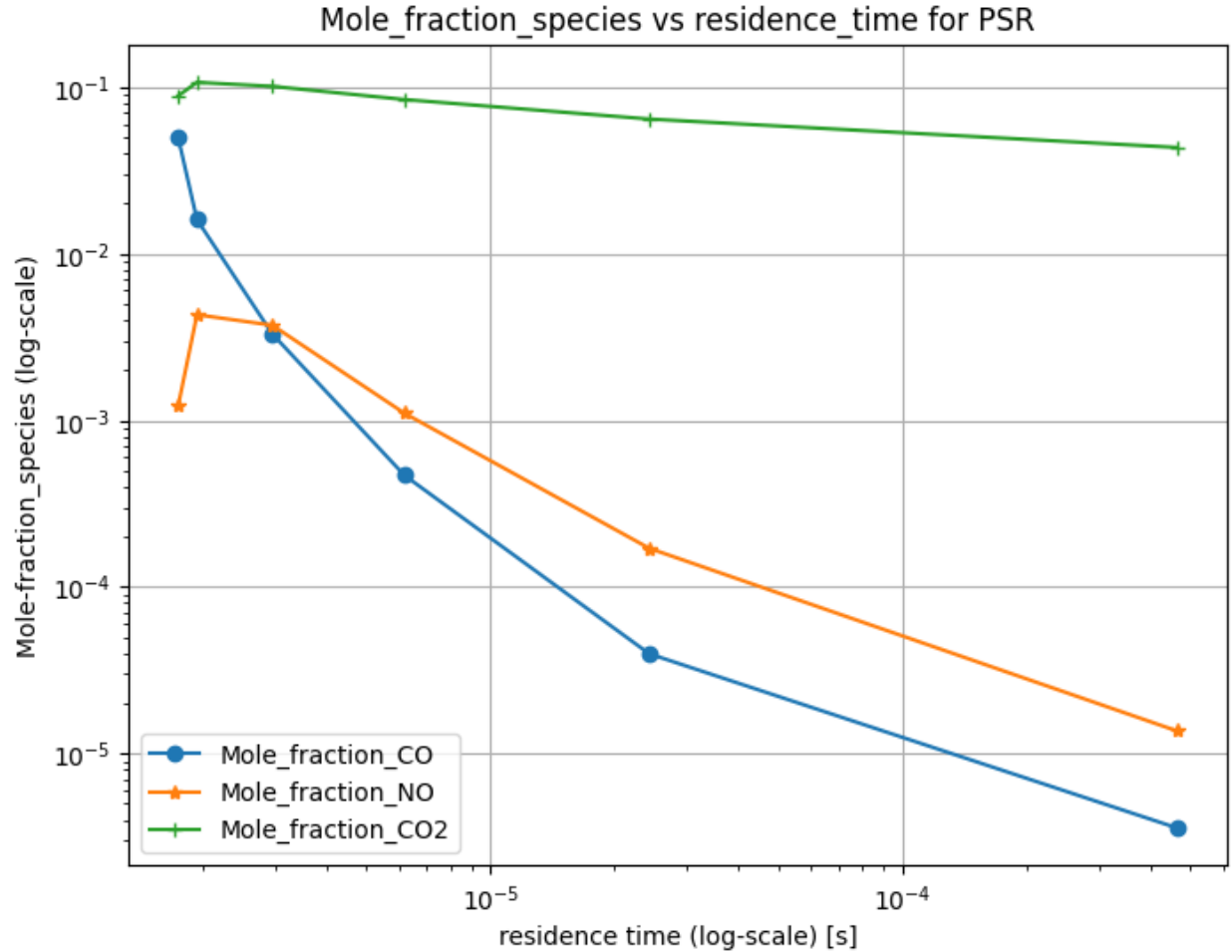


Fig 17 – Mole fraction species vs Residence time

CO mole fraction:

- As residence time decreases, there is less time for complete combustion reactions to occur. If the residence time is very short, some of the reactants may not have sufficient time to participate in complete combustion, leading to the formation of incomplete combustion products such as CO.
- At power output of 350 MW when the Phi value is greater than 1, the concentration of CO increases further due to water-gas shift reaction.

NO mole fraction:

- Shorter residence times typically correspond to higher power outputs as shown in fig 16, which can result in higher flame temperatures. Elevated flame temperatures can promote the formation

of NO (nitrogen oxides) through the thermal NO<sub>x</sub> mechanism, where nitrogen from the air combines with oxygen at high temperatures.

- At power output of 350 MW when the Phi value is greater than 1, the concentration of NO decreases due to decrease in the equilibrium temperature.

CO<sub>2</sub> mole fraction:

- For CO<sub>2</sub>, the concentrations depend on the equilibrium between reactants and products. The variation in CO<sub>2</sub> mole fraction is not very high when compared to CO and NO.
- As the power output increases, the phi value shifts towards 1 allowing the reaction mixture to reach chemical equilibrium resulting in more complete combustion. Hence CO<sub>2</sub> concentration keeps on increasing.
- However, at power output of 350 MW when the Phi value is greater than 1, the concentration of CO<sub>2</sub> decreases due to water-gas shift reaction resulting in production of CO.