CL322 – Chemical Reaction Engineering

Project I – Membrane Reactor

Name: Aditya Gupte

Roll Number: 21110012

Introduction

In the industry, the water gas shift reaction is a significant and commonly used reaction. Carbon monoxide is transformed into carbon dioxide in the water gas shift process, whereas hydrogen is created from water or steam. The development of hydrogen energy and carbon capture and storage for the purpose of producing alternative fuels and reducing the greenhouse effect in the atmosphere has led to advancements over time in these fields, and one important way to meet the needs of both is through the water gas shift reaction, which enhances CO2 capture while also producing hydrogen. This reaction is also an important step in the Bosch process, which is a large-scale method to produce Hydrogen gas [1]. The reaction is represented as follows:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Explaining the Problem Statement:

It is generally known that by appropriately changing the local concentration of the reactants involved, reaction networks may be made more selective towards a target product. By connecting a membrane separation unit to the reactor, it is possible to specifically modify the reactant's and/or product's concentration. The reactor and membrane are mostly coupled together in the same unit to achieve a greater amount of conversion [2].

For the analysis, we are using a Plug Flow Reactor (PFR), which has a Hydrogen-selective permeable membrane that allows us to remove Hydrogen gas. It is removed along the length of the reactor. This causes the equilibrium to shift, which triggers the reaction in the forward direction (details in the Results section). As a result, there is increased production of H_2. For solving the concentration profile, the most common assumption made is that the given reaction is elementary.

According to Fick's law of diffusion, the molar flux due to diffusion is proportional to the concentration gradient. The second derivative of concentration with space determines how quickly the concentration of the solution changes at a given position in space [3].

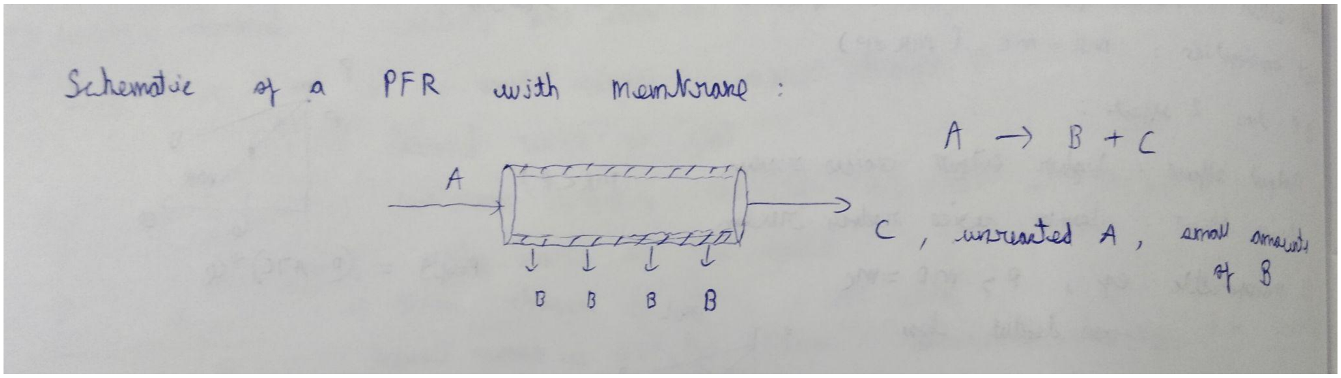

Fig 1: A schematic of PFR with membrane

Approach and Calculations:

First, from the reaction, we get the rate law. To determine the concentration profiles and approach the problem, there are some assumptions to aid in the calculation, and this will allow us to solve the problem further.

1. Reaction is elementary
2. The volume of the PFR is constant
3. The membrane in PFR is only permeable to Hydrogen gas; hence, no other gas will be removed along the length.
4. Values of initial concentrations of all gases, rate constants, the rate at which Hydrogen gas permeates, time frame in which we record the concentration profile., and other necessary assumptions to solve the ODE's numerically.

Other assumptions made will be mentioned during the calculations.

Fig 2: Reaction and reactor design:

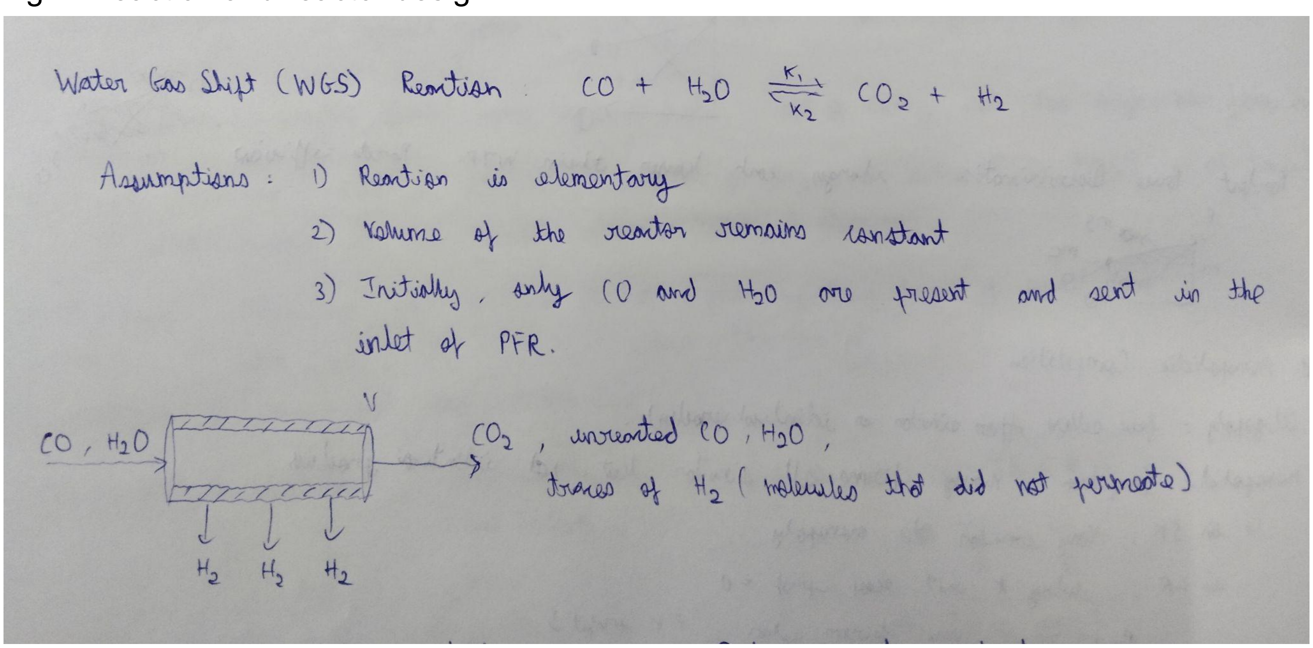

Fig 3: Defined Variables:

K_1 : Forward rate constant , K_2 : Backward rate constant

V : Volume of the reactor (constant)

r_{CO} : rate of consumption of CO

r_{H_2O} : rate of consumption of H_2O

r_{CO_2} : rate of production of CO_2

r_{H_2} : rate of production of H_2

$r_{H_2,P}$: rate of permeation of H_2 from membrane

Fig 4: Rate law of components:

From stoichiometry, $\frac{r_{CO}}{-1} = \frac{r_{H_2O}}{-1} = \frac{r_{CO_2}}{1} = \frac{r_{H_2}}{1}$

$$r_{CO} = -K_1 C_{CO} C_{H_2O} + K_2 C_{CO_2} C_{H_2}$$

$r_j = \frac{1}{V}\frac{dN_j}{dt}$ $\quad j \rightarrow$ element

if V is constant, $r_j = \frac{d(N_j/V)}{dt} = \frac{dC_j}{dt}$ $\quad C_j$: concentration of element j

Concentration is defined as the ratio of the number of moles of the component to the volume occupied by it. Since we have assumed that the volume of PFR is constant, we take the V inside the differential so that N/V becomes C(concentration). Hence, we can write the rate as the rate of change of concentration of the component with time. While we use partial pressure in the rate law, since volume is constant, we can replace it with the concentration term, which we get from PV=NRT. The constant term is adjusted with the rate constant value.

Fig 5: Continuation of rate law determination

Hence, we can write the rate law as :

$$\frac{dC_{CO}}{dt} = -k_1 C_{CO} C_{H_2O} + k_2 C_{CO_2} C_{H_2} \quad - (1)$$

Similarly,

$$\frac{dC_{H_2O}}{dt} = -k_1 C_{CO} C_{H_2O} + k_2 C_{CO_2} C_{H_2} \quad - (2)$$

$$\frac{dC_{CO_2}}{dt} = k_1 C_{CO} C_{H_2O} - k_2 C_{CO_2} C_{H_2} \quad - (3)$$

Since H_2 is permeating out from the membrane, we also need to consider the rate at which H_2 is permeating.

$$r_{H_2, perm} = -D_{H_2} * \frac{dC_{H_2}}{dt} \rightarrow \text{Fick's law of diffusion}$$

D_{H_2} : diffusivity of Hydrogen through membrane

D_{H_2} (at room temp.) $= 2.38 \times 10^{-1}\ cm^2/s$

To ease the solving of ODE further, I have assumed the value of rate of permeation of H_2. In the attached code, $r_{H_2, p} = 0.01$

$$\Rightarrow r_{H_2} = k_1 C_{CO} C_{H_2O} - k_2 C_{CO_2} C_{H_2} - r_{H_2, p} = \frac{dC_{H_2}}{dt} \quad - (4)$$

As we remove the Hydrogen gas from the membrane, its concentration decreases in the PFR. According to the rate law obtained, to achieve equilibrium, the forward reaction will be favoured. Thus, a greater amount of CO_2 and H_2 will be produced as compared to when H_2 is not removed by the membrane.

Thus, we have obtained our 4 ODEs. They are written as follows:

Fig 6: Rate law equations and its relation with concentrations of each component

$$\frac{dC_{CO}}{dt} = -k_1 C_{CO} C_{H_2O} + k_2 C_{CO_2} C_{H_2} \quad - (1)$$

$$\frac{dC_{H_2O}}{dt} = -k_1 C_{CO} C_{H_2O} + k_2 C_{CO_2} C_{H_2} \quad - (2)$$

$$\frac{dC_{CO_2}}{dt} = k_1 C_{CO} C_{H_2O} - k_2 C_{CO_2} C_{H_2} \quad - (3)$$

$$\frac{dC_{H_2}}{dt} = k_1 C_{CO} C_{H_2O} - k_2 C_{CO_2} C_{H_2} - r_{H_2,P} \quad - (4)$$

Solve simultaneously using the Runge-Kutta method.
4 ODEs

These 4 ODEs have been solved simultaneously using the Runge-Kutta method. I have solved these numerically by writing the code in Python. All the assumed values are shown in the below figure.

Initial Values:

Time-frame : 0 to 20 s

~~kt~~ $k_1 = 1.324 \ m^3/mol\text{-}s$

$k_2 = 1.627 \ m^3/mol\text{-}s$

$r_{H_2,P} = 0.01 \ mol/m^3\text{-}s$

$C_{j,i} \rightarrow$ initial conc^n of element j

$\Rightarrow C_{CO,i} = 5$ mol $\quad C_{CO_2,i} = 0$ mol

$C_{H_2O,i} = 5$ mol $\quad C_{H_2,i} = 0$ mol

Fig 7: Assumed values and constants in the code

The code has been attached along with the report. I have also mentioned the link that will take to the Google collab on which the code is implemented.

Numpy and matplotlib libraries have been used to solve the integration and plot the graphs, respectively.

Results:

For the specified initial conditions, the following image depicts the concentration profiles of each component.

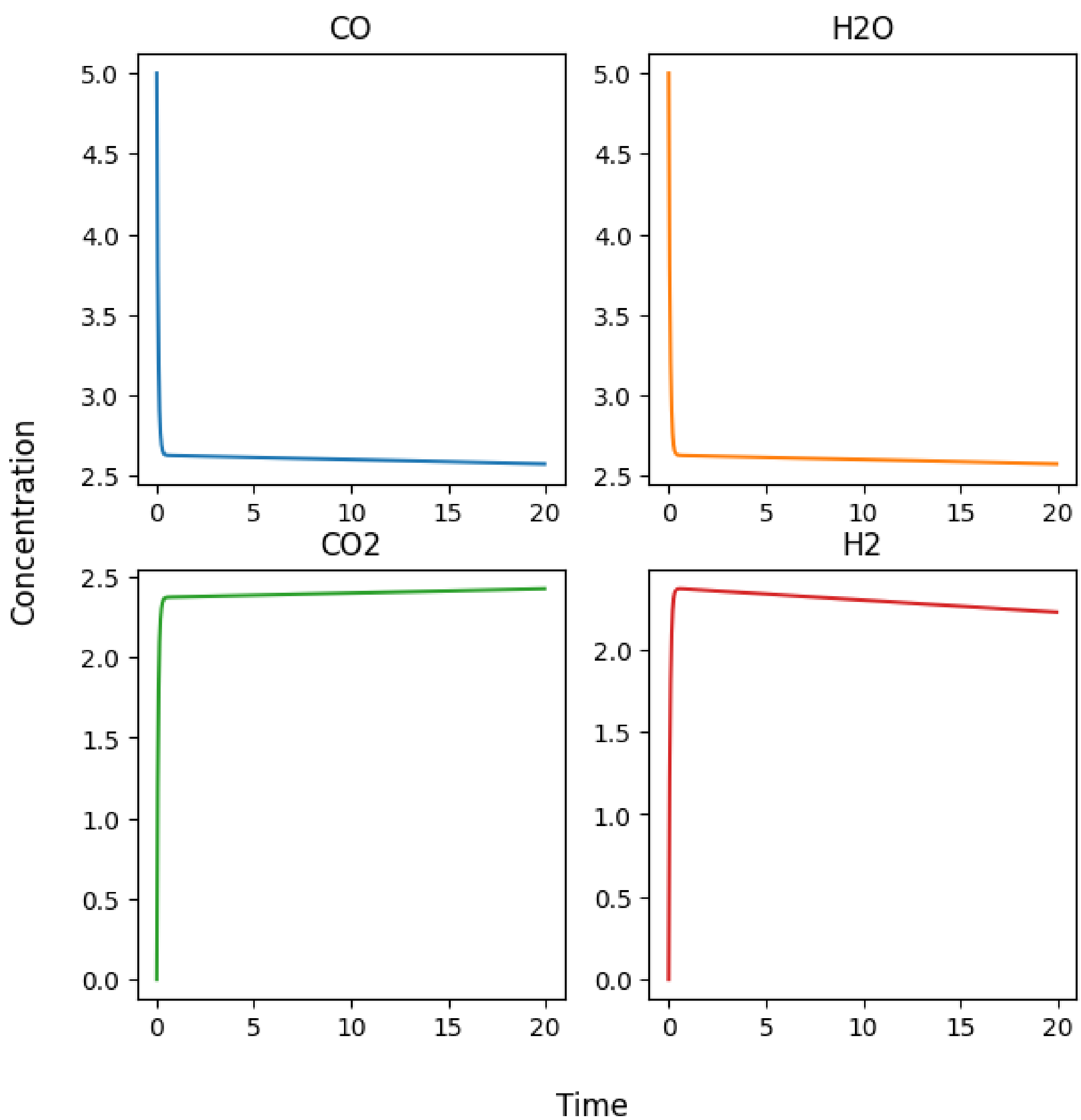

Fig 8: Plot of concentration profile of each component for specified initial conditions w.r.t. time

Suppose the initial concentration of the reactants is not equal; we get the following concentration profile:

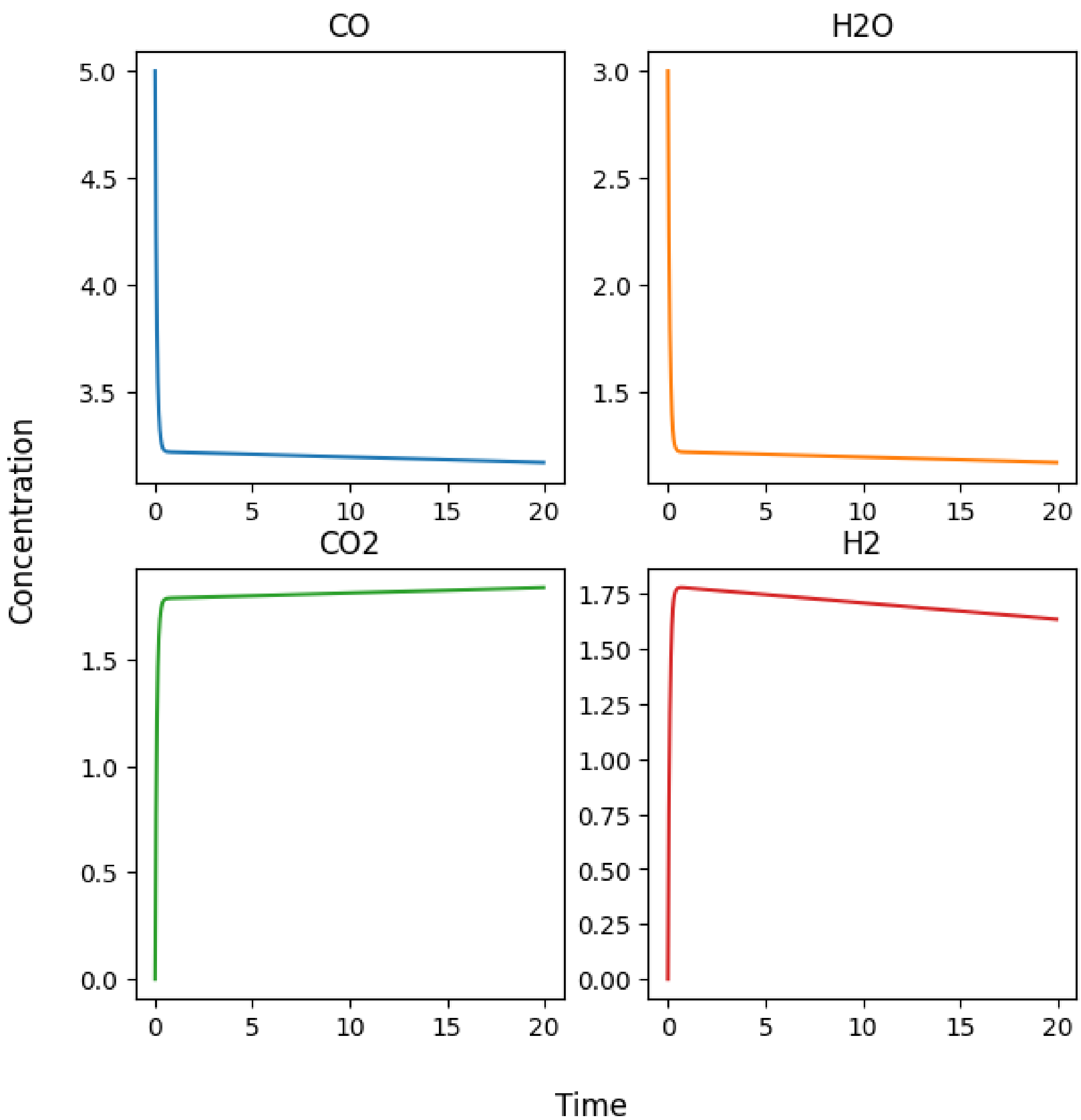

Fig 9: Plot of the concentration profile of each component when [CO]i = 5 mol, [H20]i = 3 mol w.r.t. time

Suppose the initial concentration of the reactants is the same, but the rate of permeation=0.1; we get the following concentration profile:

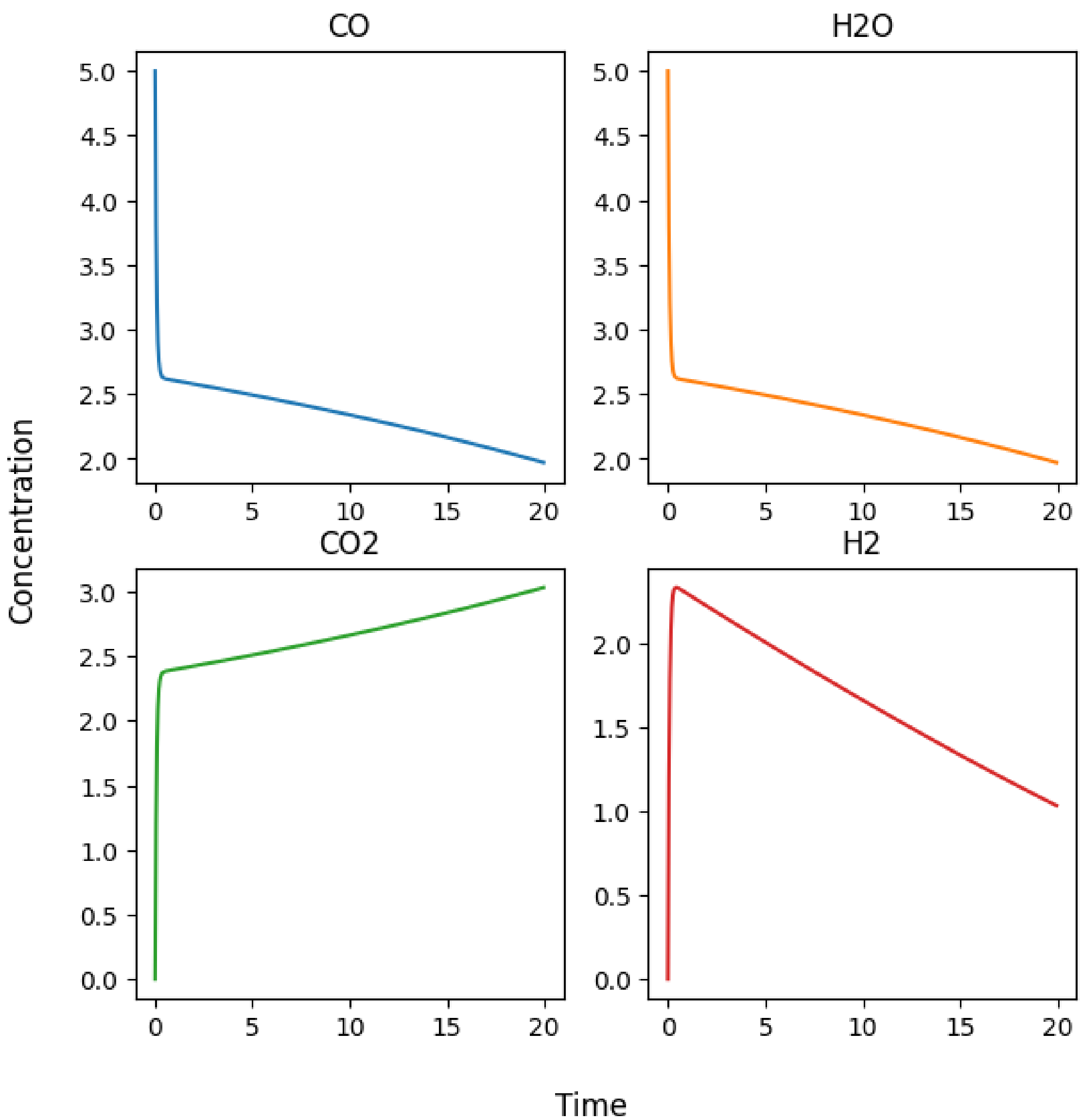

Fig 10: Plot of the concentration profile of each component when r_permeaion = 0.1 with other conditions remaining the same w.r.t. time.

Suppose there is some initial concentration of Hydrogen gas in the reactor, then the concentration profile is depicted as:

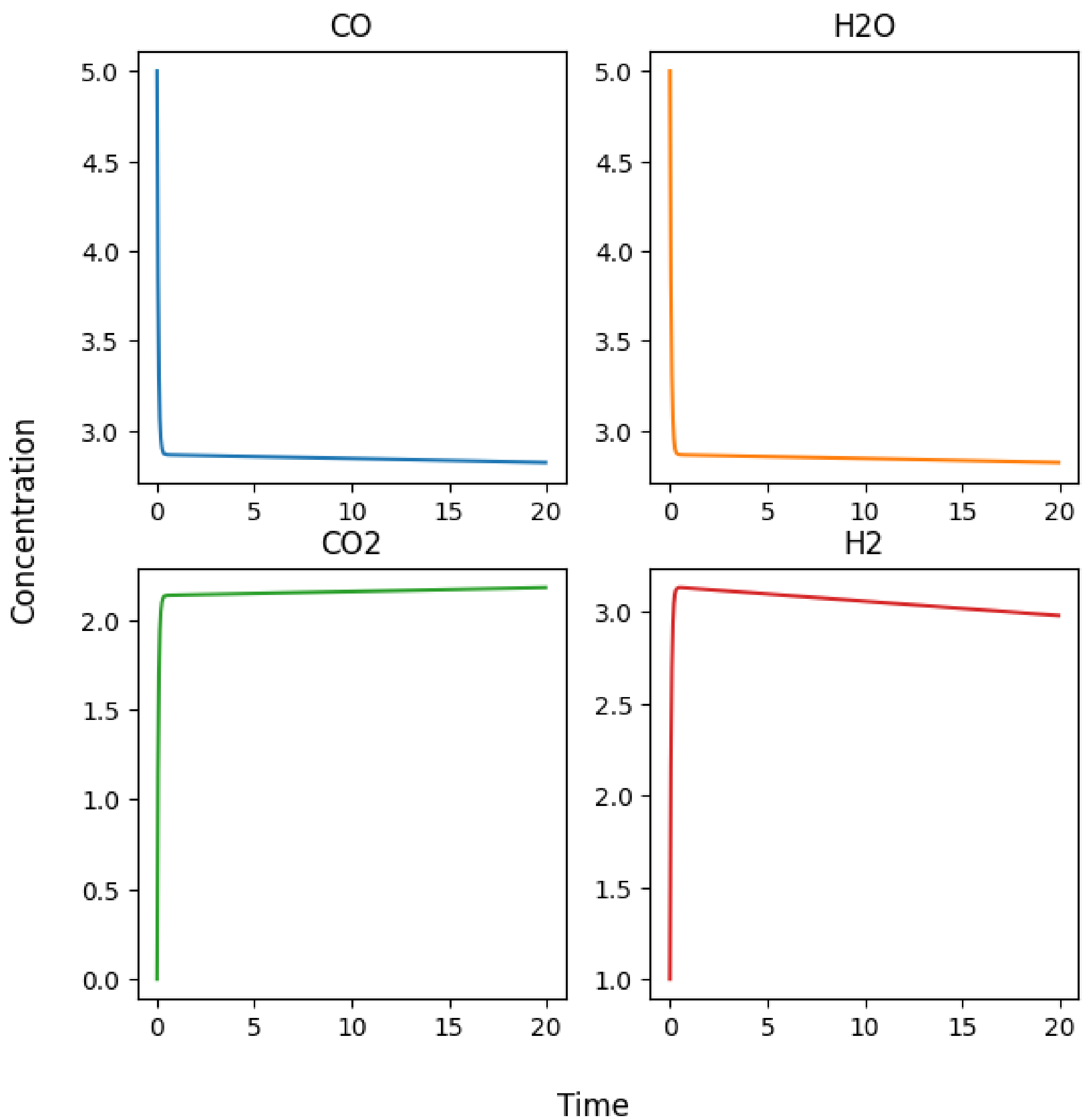

Fig 11: Plot of the concentration profile of each component when [H2]i = 1 mol with other conditions remaining the same w.r.t. time

Suppose the Hydrogen gas was not permeated from the reactor, then the concentration profile is depicted as:

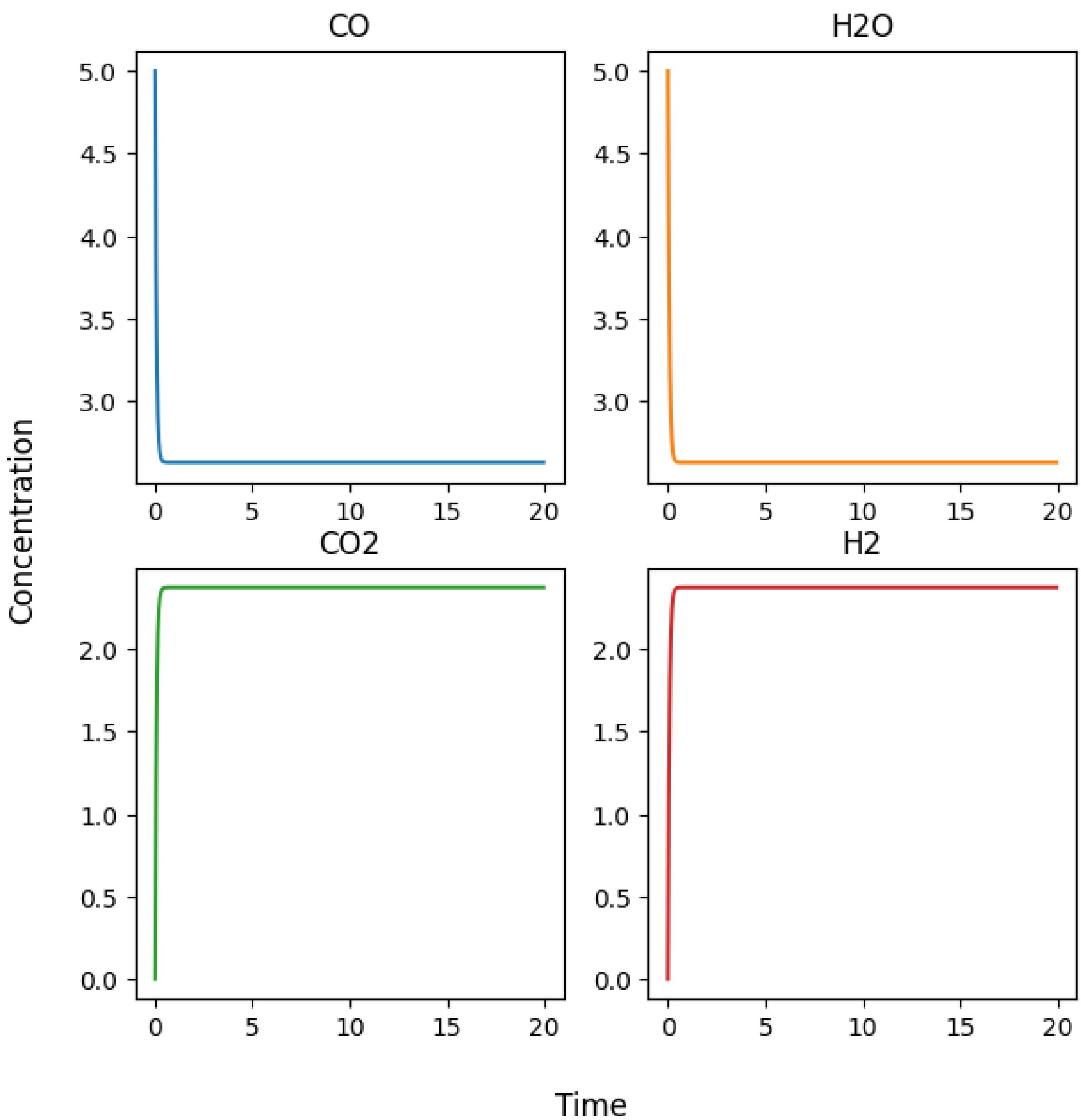

Fig 12: Plot of the concentration profile of each component when Hydrogen gas is not permeated from the reactor with other conditions remaining the same w.r.t. time

A general trend observed within the first 4 plots is that the concentration of CO_2 has increased due to the permeation of H_2. As we remove H_2, its concentration starts decreasing after the bend, whereas the concentration of CO_2 increases gradually after the bend. This is the primary difference caused by the use of membranes in PFR. This has increased the production of gas for various applications. Maybe if the permeated H_2 is collected and used again through a recycle tube, then we can boost the production of the products by reutilizing the H_2 gas.

Conclusion

The Water Gas Shift (WGS) reaction is an important reaction widely used in industries. It is a critical step in the Bosch process. This reaction has several applications. It is important to study the kinetics of the reaction in order to understand it. Some of its useful applications are as follows:

1. Hydrogen Production: The WGS reaction is a crucial step in the production of Hydrogen gas. CO and water react to form hydrogen and carbon dioxide. Hydrogen is a clean and versatile energy carrier. Hence, it is also widely used in fuel cells, ammonia production, hydrogenating hydrocarbons, etc.

2. Fuel Production: Hydrogen gas is an important feedstock in various chemical processes, including the production of fuels like methanol and synthetic hydrocarbons.

3. Environmental Benefits: CO is a toxic gas and is one of the harmful gases that causes Greenhouse emissions. This reaction is used in industrial processes to convert CO, such as the conversion of natural gas to syngas.

4. Chemical Process Engineering: The WGS reaction is a reversible reaction and can be used to gain insights and understanding about reactor design and optimizing the conversion. The use of membranes in reactors is innovative and can be used in other reactions as well. This reaction can be used as a basis to apply this concept in further complicated processes [4].

References

[1] https://www.sciencedirect.com/science/article/abs/pii/S0306261919317659
[2] https://www.sciencedirect.com/topics/chemical-engineering/membrane-reactor
[3] https://byjus.com/physics/ficks-law-of-diffusion/#:~:text=According%20to%20Fick's%20law%20of,derivative%20of%20concentration%20with%20space.
[4] https://en.wikipedia.org/wiki/Water%E2%80%93gas_shift_reaction#:~:text=7%20References-,Applications,in%20the%20production%20of%20hydrogen.