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CPJ 421 Reactor

Modeling and Design of the Reverse Water-Gas Shift Reactor

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Executive summary

This report presents the design of a reverse water-gas shift (RWGS) reactor for the conversion of carbon dioxide (CO_2) to carbon monoxide (CO) using hydrogen (H_2). The reactor design is based on a fixed-bed, multi-tubular, non-adiabatic, non-isothermal configuration, utilising a $Ni/MgAl_2O_4$ catalyst to achieve a 20 % conversion of CO_2. The reactor is placed in a gas-fired furnace to supply the necessary heat, operating at 723 K to 1100 K to minimise methane formation.

The final design specifications of the reactor and the furnace are included in Table 2. The feed conditions to the reverse water-gas shift reactor (RWGS) are included in Table 1. The multitubular packed-bed reactor, heated in a gas-fired furnace, achieved a 79.6 % conversion of CO_2 into CO.

The optimisation process considered various parameters such as catalyst particle size, tube diameter, bed porosity, and reactor pressure, such that the final design achieved minimal pressure drop while maintaining a realistic design. Materials for reactor construction were selected to withstand high operating temperatures and pressures, with Inconel 601 chosen for its durability and resistance to hydrogen embrittlement.

Table 1: Feed specifications of the RWGS reactor.

Parameter	Value
Total mass flow rate $(kg\,s^{-1})$	56.6
Total molar flow rate $(mol\,s^{-1})$	6034.73
Molar flow rate $(mol\,s^{-1})$	
CO_2 molar frac	0.171
CO molar frac	0.007
H_2 molar frac	0.822
Temperature (K)	723
Pressure (kPa)	400

Table 2: Final design specifications for the fixed-bed, multi-tubular, non-adiabatic, non-isothermal reactor, heated by a gas-fired furnace.

Parameter	Specification	Units
Number of Tubes	1000	-
Tube Diameter	0.08	m
Tube Length	1.27	m
Catalyst Type	$Ni/MgAl_2O_4$	-
Total Catalyst Mass	3000	kg
Bed Density (ρ_B)	471	$kg\,m^{-3}$
Catalyst Density (ρ_c)	2355.2	$kg\,m^{-3}$
Bed Porosity (ϵ)	0.8	-
Catalyst Diameter (d_p)	0.006	m
MHSV	67.9	h^{-1}
Tube Material	Inconel 601	-
Furnace Material of Construction	Refractory brick with carbon steel shell	-
Furnace Size	4.76 x 2.52 x 2.27	m
Furnace Duty	90.52	MW
Furnace shell insulation	Calcium silicate	-

Contents

Nomenclature

$\dot{m}$ Mass flow rate, $\mathrm{kg\,s^{-1}}$

$\dot{n}$ Molar flow rate, $\mathrm{mol\,s^{-1}}$

η Effectiveness factor, dimensionless

ρ_B Reactor bed density, $\mathrm{kg\,m^{-3}}$

ρ_c Catalyst density, $\mathrm{kg\,m^{-3}}$

C_i Concentration of species i, $\mathrm{mol\,m^{-3}}$

d_p Catalyst particle diameter, m

D_t Reactor tube diameter, m

$E_{a,j}$ Activation energy for reaction j, $\mathrm{J\,mol^{-1}}$

F_i Molar flow rate of species i, $\mathrm{mol\,s^{-1}}$

K_i Adsorption constant for species i at a given temperature, units are species-specific

K_j Equilibrium constant of reaction j at a given temperature, units are species-specific

k_j Catalyst mass-based rate constant for reaction j at a given temperature, $\mathrm{mol\,kg^{-1}\,s^{-1}}$

$K_{0,i}$ Adsorption pre-exponential constant for species i, units are species-specific

$k_{0,j}$ Catalyst mass-based Arrhenius pre-exponential constant for reaction j, $\mathrm{mol\,kg^{-1}\,s^{-1}}$

L Reactor tube length, m

P Pressure in the reactor, Pa

r_i Catalyst mass-based rate of species i, $\mathrm{mol\,kg^{-1}\,s^{-1}}$

R_j Catalyst mass-based rate of reaction j, $\mathrm{mol\,kg^{-1}\,s^{-1}}$

T Temperature in the reactor, K

u Superficial velocity, $\mathrm{m\,s^{-1}}$

W Catalyst mass, kg

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1 Introduction

The production of synthetic fuels, particularly Jet-A1 kerosene, has gained significant importance as the global demand for cleaner and more sustainable energy sources increases. In the context of this project, a comprehensive synthetic fuel processing plant has been designed to produce $0.93 \, \mathrm{kg \, s^{-1}}$ of Jet-A1 kerosene. The process includes the Reverse Water-Gas Shift (RWGS) reactor, for increasing the efficiency of carbon conversion and reducing the environmental impact of the production process.

The function of the RWGS reactor is to capture and convert carbon dioxide (CO_2), from flue gases generated during the production of synthetic fuels. By converting CO_2 into carbon monoxide (CO) through reaction with hydrogen (H_2), the reactor not only contributes to the production of synthesis gas (syngas) but also reduces the overall CO_2 emissions of the plant.

The RWGS reactor has been designed to integrate with the larger processing plant, by using the flue gas as a feedstock to convert waste CO_2 into syngas for the Fischer-Tropsch synthesis of hydrocarbons.This report details the design, optimisation, and operational parameters of the RWGS reactor, contributing to supporting sustainable synthetic fuel production by increasing carbon conversion efficiency and minimising greenhouse gas emissions.

2 Reactor model

2.1 Kinetics and mass tansfer

The reverse water-gas shift (RWGS) reactor is modelled as a packed bed reactor (PBR), with several assumptions. The gases behave as ideal gases and the reactor operates under steady-state conditions. One-dimensional plug flow is assumed, meaning that all the gas particles flow with the same direction and velocity without back-mixing, with composition and temperature only varying in the axial direction. Hence, radial heat and mass transfer are neglected. These assumptions are true of a reactor with high linear velocities and small diameter tubes, that operates at low to moderate temperature and pressure.

To model the reactions occurring in the RWGS reactor, the kinetic model relies on three reactions: steam reforming of methane, methanation, and the reverse water-gas shift reaction. These reactions cover the primary transformations needed for synthesis gas

(syngas) production, and all major side reactions, given the feed composition specified in Table 1.

- **Steam reforming of methane:**

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_{298}^\circ = 206.3\,\text{kJ/mol} \tag{1}$$

- **Methanation:**

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H_{298}^\circ = 164.9\,\text{kJ/mol} \tag{2}$$

- **Water-gas shift:**

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298}^\circ = -41.1\,\text{kJ/mol} \tag{3}$$
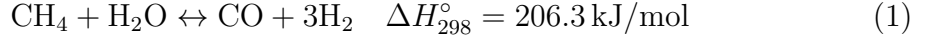
Xu and Froment, 1989 obtained the intrinsic kinetics for reactions 1, 2 and 3, the rate equations of which, are represented by Equations 4, 5 and 6, respectively. The kinetics were obtained experimentally using a $Ni/MgAl_2O_4$ catalyst, with particle diameters of 0.18 mm—0.25 mm.
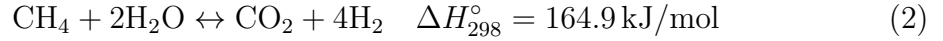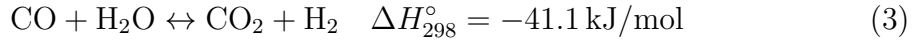
$$R_1 = \frac{k_1}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_I} \right) \times \frac{1}{\phi^2} \quad \left[\text{mol}\,\text{kg}^{-1}\,\text{s}^{-1} \right] \tag{4}$$

$$R_2 = \frac{k_2}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{II}} \right) \times \frac{1}{\phi^2} \quad \left[\text{mol}\,\text{kg}^{-1}\,\text{s}^{-1} \right] \tag{5}$$

$$R_3 = \frac{k_3}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{III}} \right) \times \frac{1}{\phi^2} \quad \left[\text{mol}\,\text{kg}^{-1}\,\text{s}^{-1} \right] \tag{6}$$

$$\phi = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} \frac{p_{H_2O}}{p_{H_2}} \tag{7}$$

The equations and associated parameters derived by Xu and Froment, 1989 are well outlined and discussed in Rahimpour et al., 2012. The Arrhenius equation, Equation 9, is used to calculate the mass based reaction rates, using the kinetic parameters included in Table 3.

Table 3: Arrhenius parameters for reactions, taken from Rahimpour et al., 2012 and converted to SI.

Reaction, j	k_{0j} (mol/(kg$_{\text{cat}}$·s))	E_{aj} (J/mol)
1 (Steam Reforming)	3.7×10^{17} (Pa$^{0.5}$)	240100
2 (Methanation)	8.95×10^{16} (Pa$^{0.5}$)	243900
3 (Water-Gas Shift)	5.43 (Pa^{-1})	67130

In this model, adsorption refers to the process by which reactant molecules adhere to the active sites on the catalyst's surface. This is considered because it directly impacts the availability of reactants for the chemical reaction; only molecules adsorbed onto the catalyst can participate in the reaction. The influence of adsorption on reaction rates is incorporated into the kinetic model through adsorption enthalpies (ΔH_i) and constants (K_{0i}), which modify the effective gas-phase partial pressures by accounting for the adsorption behavior of each species.

The model applies Langmuir adsorption isotherms to establish relationships between gas-phase concentrations and the concentrations of adsorbed species. This leads to the formulation of rate equations that include a denominator representing a balance between vacant active sites and those occupied by reactants (Xu and Froment, 1989), Equation 7. The inclusion of this denominator, which contains adsorption terms, adjusts the reaction rate based on how strongly each species adsorbs to the catalyst. This allows the model to more accurately predict the kinetics of the reactions under various operating conditions, as it accounts for the competition among species for available active sites and how this competition influences overall reaction rates.

The temperature dependance of the adsorption constants is taken into consideration by Equation 8, and the parameters to be used in this equation are included in Table 4.

$$K_i = K_{0i} \times \exp\left(\frac{-\Delta H}{RT}\right) \tag{8}$$

$$k_j = k_{0j} \times \exp\left(\frac{-E_j}{RT}\right) \tag{9}$$

Table 4: Van't Hoff Parameters for species adsorption, taken from Rahimpour et al., 2012 and converted to SI.

Species	K_{0i} $(\mathbf{Pa^{-1}})$	ΔH_i $(\mathbf{J/mol})$
CH_4	6.65×10^{-9}	-38280
CO	8.23×10^{-10}	-70650
H_2	6.12×10^{-14}	-82900
H_2O	1.77×10^5	88680

Finally, the equilibrium constants (K_j) are temperature dependant and are calculated for each reaction j, using Equations 10, 11 and 12 (Rahimpour et al., 2012).

$$K_I = \exp\left(\frac{-26830}{T_s} + 30.114\right) \times 10^{10} \quad \left[\text{Pa}^2\right] \tag{10}$$

$$K_{II} = K_I \cdot K_{III} \quad \left[\text{Pa}^2\right] \tag{11}$$

$$K_{III} = \exp\left(\frac{4400}{T_s} - 4.036\right) \tag{12}$$

The net rate equations for for each species, i, is presented by Equation 15, 16, 17, 18 and 19. Effectiveness factors (η_j) account for the internal mass transfer effects that limit each reaction, j. These factors were incorporated into the model by De Groote and Froment, 1996, for the Ni/MgAl$_2$O$_4$ catalyst, with a particle diameter of 5 mm at an average reactor temperature of 900 °C. The effectiveness factors η_1, η_2 and η_3 were given as 0.07, 0.06 and 0.7, respectively. Internal diffusion rates into a solid catalyst particle are influenced by the diameter of the catalyst particle and the temperature of the reactor.

$$\Phi_j = \sqrt{\frac{k'\rho_c C_{A_s}^{n-1} d_p^2}{4D_e}} \tag{13}$$

$$\eta_j = \eta_{j,ref} \cdot \exp\left(\frac{E_{a,j}}{2R}\left(-\frac{1}{T} + \frac{1}{T_{\text{ref}}}\right)\right) \cdot \frac{d_{p,\text{new}}}{d_{p,\text{ref}}} \tag{14}$$

The differences in temperature and catalyst particle diameter between the design discussed in this report and that in De Groote and Froment, 1996, will be accounted for using Equation 14. This is a proration of η_j derived from the inverse proportionality between η_j and the Thiele modulus (Φ) described by Fogler, 2005. The equation for Φ is included as Equation 13.

$$r_{\text{CH}_4} = -\eta_1 R_1 - \eta_2 R_2 \tag{15}$$

$$r_{\text{H}_2} = 3\eta_1 R_1 + 4\eta_2 R_2 + \eta_3 R_3 \tag{16}$$

$$r_{\text{H}_2\text{O}} = -\eta_1 R_1 - 2\eta_2 R_2 - \eta_3 R_3 \tag{17}$$

$$r_{\text{CO}} = \eta_1 R_1 - \eta_3 R_3 \tag{18}$$

$$r_{\text{CO}_2} = \eta_2 R_2 + \eta_3 R_3 \tag{19}$$

The mass balance equations, based on catalyst mass, for each species in the PBR, are depicted below as Equation 20, 21, 22, 23 24.

$$\frac{d\text{CH}_4}{dW} = r_{\text{CH}_4} \tag{20}$$

$$\frac{d\text{H}_2}{dW} = r_{\text{H}_2} \tag{21}$$

$$\frac{d\text{H}_2\text{O}}{dW} = r_{\text{H}_2\text{O}} \tag{22}$$

$$\frac{d\text{CO}}{dW} = r_{\text{CO}} \tag{23}$$

$$\frac{d\text{CO}_2}{dW} = r_{\text{CO}_2} \tag{24}$$

The external mass transfer effects were assumed to be negligible. The validity of this assumption was be verified during the modeling procedure, by calculating the Mears' criterion using Equation 25, which assesses the significance of mass transfer resistances compared to the intrinsic kinetics of the reaction. Several dimensionless numbers are required to calculate the Mears' criterion, given that the external mass transfer coefficient, k_c, is unknown. These dimensionless numbers are calculated using Equations 26, 28 and 29.

$$\text{Mears Criterion} = \frac{r_i d_p 0.5 RT}{P_{A,b} k_c \rho_B} \leq 0.15 \tag{25}$$

$$Re = \frac{\rho u d_p}{\mu} \tag{26}$$

$$D_{\text{A,mix},T,P} = D_{\text{A,mix},T_{ref},P_{ref}} T_{ref} \left(\frac{T}{T_{ref}}\right)^{\frac{3}{2}} \left(\frac{P_{ref}}{P}\right) \tag{27}$$

$$Sc = \frac{\mu}{\rho D_{AB}} \tag{28}$$

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \tag{29}$$

$$k_c = \frac{Sh D_{AB}}{d_p} \tag{30}$$

The check will be performed for CO_2 only, this molecule is the largest and has the highest molecular weight making it most likely to have the lowest diffusivity compared to the other species. Thus, the external mass transfer limitations of the other reacting species can be neglected in the case that the Mears' number for CO_2 is less than 0.15. This indicates that external mass transfer limitations are negligible, and the observed reaction rate is controlled by the intrinsic kinetics of the reaction. In such a case the assumption to neglect external mass transfer is validated.

The diffusivity of CO_2 at 1 atm and 273 K ($D_{\text{CO}_2,\text{mix},T,P}$) is $2.17\,\text{m}^2\,\text{s}^{-1}$ (Wolf et al., 2016). Equation 27 will be used to calculate the diffusivity of CO_2 at the reactor temperature and

pressure, at each iteration during the numerical solution of the mass balance equations.

2.2   Energy balance and pressure drop

The pressure drop along the length of the reactor was calculated using the Ergun equation, Equation 35, note that the pressure drop is per kg of catalyst. Pressure drop will be calculated per tube of the reactor, thus the total mass flux and molar flow divided by the number of tubes will be used in the calculation. The average molecular mass of the gasses is the sum of the mole fractions multiplied by the respective molar mass of each component. The Ergun constant, K_w, is calculated with Equation 34 and represents the pressure drop per kg of catalyst. The value of K_w will be considered when making design decisions on catalyst size, bed density, bed porosity, tube diameter and number of tubes, providing insight into the feasibility of the design in the context of pressure drop.

$$G = \frac{M_{\text{tube}}}{A_c} \tag{31}$$

$$\rho_0 = \frac{MM_{\text{avg}}P_0}{RT_0} \tag{32}$$

$$\rho_B = \rho_c(1 - \epsilon) \tag{33}$$

$$K_W = -\frac{G}{A_c\rho_0\rho_B d_p}\left(\frac{1-\epsilon}{\epsilon^3}\right)\left(150\mu_0\frac{1-\epsilon}{d_p} + 1.75G\right) \tag{34}$$

$$\frac{dP}{dW} = K_W\frac{P_0 F_t T}{P F_{0,t} T_0} \tag{35}$$

The viscosity of the gas, μ, will be assumed constant at that of the inlet gaseous mixture and conditions, in order to simplify the calculation. This viscosity will be found using DWSIM. The catalyst density was reported by Santos et al., 2023 as $2355.2\,\text{kg m}^{-3}$.

Due to the endothermic nature of the reactions occurring in the RWGS reactor, heat is required to sustain the chemical reactions occuring. Furthermore, methane formation is favoured at lower temperatures, which is an undesirable by-product due to its consumption of H_2 and its high global warming potential. Methane is stable at temperatures below 700 °C, thus the reactor temperature needs to be maintained above 700 °C in order to shift the equilibrium towards producing CO (Wolf et al., 2016).

Similarly to catalytic steam reforming using nickel-aluminium, the heat required to maintain the required temperature can be serviced by the radiative zone of a gas-fired service

(Xu and Froment, 1989). The generalised energy balance for a non-isothermal and non-adiabatic PBR is represented by Equation 39, where Q is calculated using Equation 37 and has units of $W \, kg^{-1}$ of catalyst.

$$\sum_{j=1}^{m} \Delta H_{\text{rx},j} \cdot r_j = \sum_{j=1}^{m} (\Delta H_{\text{Rx},j,298} + \Delta C_{p,\text{rx},j} \cdot (T - T_{\text{ref}})) \cdot r_j \tag{36}$$

$$Q = U \cdot \frac{a}{\rho_B} \cdot (T_u - T) \tag{37}$$

$$a = \frac{4}{D_t} \tag{38}$$

$$\frac{dT}{dW} = \frac{Q - \sum_{j=1}^{m} \Delta H_{\text{rx},j} \cdot r_j}{\sum_{i=1}^{n} F_i C_{p,i}} \tag{39}$$

Radiative heat flux is calculated using Equation 40, which has units of $W \, m^{-2}$. Therefore this equation needs to be adjusted to be dimensionally consistent with the units of Q, in Equation 37, before being integrated into the energy balance. Hence, Equation 41 is derived from Equation 40 and has units of $W \, kg^{-1}$ of catalyst. T_u is the utility temperature, which is 2200 K, the the adiabatic flame temperature of a hydrocarbon (Seider et al., 2009).

$$\dot{q}_r = \dot{\epsilon} \cdot \sigma \cdot (T_u^4 - T^4) \tag{40}$$

$$Q_r = \frac{\dot{\epsilon} \cdot \sigma \cdot (T_u^4 - T^4) \cdot 4}{D_t \cdot \rho_B} \tag{41}$$

Where, $\dot{\epsilon}$ is the absorptivity of the material of the outer surface of the reactor tubes and σ is the Stefan-Boltzman constant ($5.670 \times 10^{-8} \, W \, m^{-2} \, K^{-4}$). The generalised energy balance expanded specifically to the reacting system discussed in this design is presented below. The C_p values of each component were accessed using the CoolProp library (Bell

et al., 2014) through its python API, at the relevant temperature and pressure.

$$\Delta C_{p,\text{rx},1} = \sum_i \nu_{\text{steam reforming},i} \cdot C_{p,i} \tag{42}$$

$$\Delta C_{p,\text{rx},2} = \sum_i \nu_{\text{methanation},i} \cdot C_{p,i} \tag{43}$$

$$\Delta C_{p,\text{rx},3} = \sum_i \nu_{\text{RWGS},i} \cdot C_{p,i} \tag{44}$$

$$\Delta H_{\text{rx},1} = \Delta H_{\text{Rx},1,298} + \Delta C_{p,\text{rx},1} \cdot (T - T_{\text{ref}}) \tag{45}$$

$$\Delta H_{\text{rx},2} = \Delta H_{\text{Rx},2,298} + \Delta C_{p,\text{rx},2} \cdot (T - T_{\text{ref}}) \tag{46}$$

$$\Delta H_{\text{rx},3} = \Delta H_{\text{Rx},3,298} + \Delta C_{p,\text{rx},3} \cdot (T - T_{\text{ref}}) \tag{47}$$

$$r_i \nu_i \Delta H_{\text{rx}} = \Delta H_{\text{rx},1} \cdot r_1 + \Delta H_{\text{rx},2} \cdot r_2 + \Delta H_{\text{rx},3} \cdot r_3 \tag{48}$$

$$\sum F_i C_{p,i} = F_{\text{CH}_4} \cdot C_{p,\text{CH}_4} + F_{\text{H}_2} \cdot C_{p,\text{H}_2} + F_{\text{H}_2\text{O}} \cdot C_{p,\text{H}_2\text{O}} + F_{\text{CO}} \cdot C_{p,\text{CO}} + F_{\text{CO}_2} \cdot C_{p,\text{CO}_2} \tag{49}$$

$$\frac{dT}{dW} = \frac{Q_r - \sum_{j=1}^m \Delta H_{\text{rx},j} \cdot r_j}{\sum_{i=1}^n F_i C_{p,i}} \tag{50}$$

The assumptions made in the energy balance model are that the utility temperature is constant, and that the outer surface temperature of the reactor tubes are equal to that of the material flowing through the reactor tubes.

3 Model solution

The profiles included in this discussion are for a single tube within the reactor, and the source code is included in the Appendix of this report.

3.1 Optimisation simulation

In the design of the reactor, an optimisation procedure was implemented to select appropriate parameters within specific bounds to ensure that the pressure drop within the reactor remains feasible. The most important parameters considered were the catalyst particle diameter and the tube diameter, other variables considered include number of tubes, bed porosity and inlet pressure. The effect of tube diameter and inlet pressure is plotted in Figure 1, lower inlet pressure and small tube diameters result in larger Ergun constants and pressure drop.
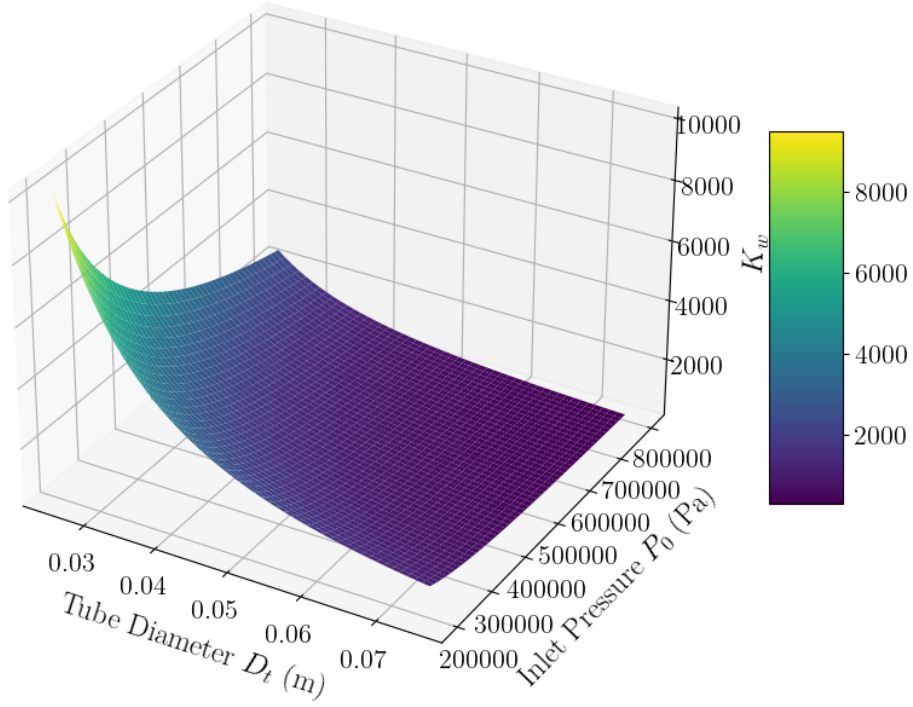
Figure 1: Three dimensional plot of the combined effect of tube diameter and inlet pressure on K_w.

As seen in Figure 2, decreasing ϵ significantly increases K_w, whereas N has relatively insignificant effects on K_w. However, more tubes results in less catalyst mass per tube and thus a lower overall pressure drop.
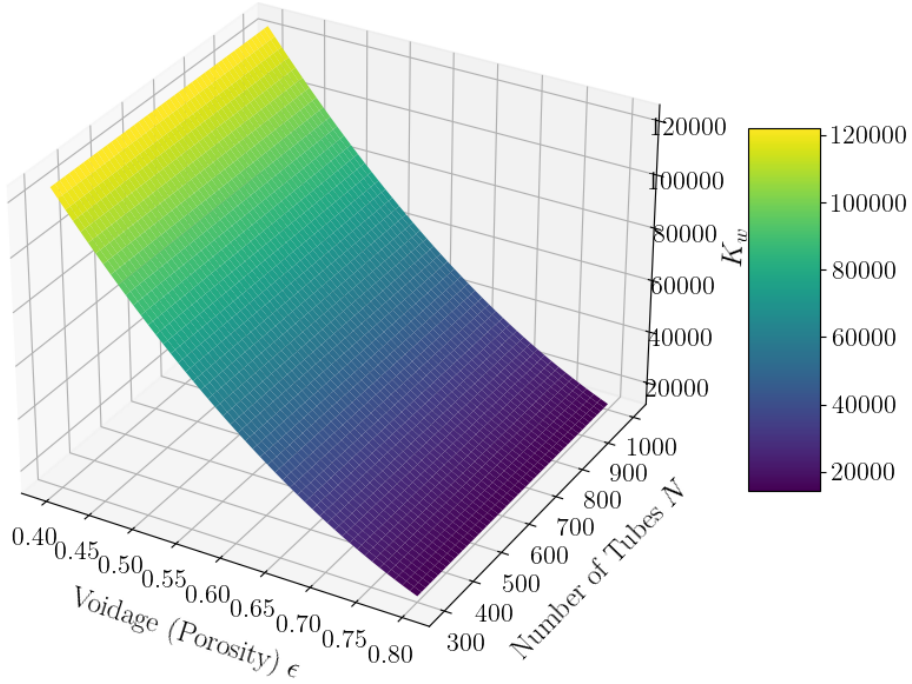
Figure 2: Three dimensional plot of the combined effect of number of tubes and bed voidage on K_w.

The catalyst particle diameter affects both mass transfer and pressure drop within the reactor. Particles larger than 6 mm were avoided as they can increase internal mass transfer resistance. Larger particles have a reduced surface area-to-volume ratio, limiting the rate at which reactants diffuse into the catalyst and products diffuse out, which can negatively impact overall reaction rates and reactor efficiency. Particles smaller than 3 mm were not considered due to the excessive pressure drop they can cause. Smaller particles increase the surface area but also create a more compact bed, leading to higher frictional resistance against fluid flow. This would result in a higher pressure drop, which is economically infeasible.

The tube diameter influences the ability to regulate temperature and pressure drop efficiently, and influences the validity of the assumption to neglect radial heat and mass transfer. Larger diameters reduce pressure drop effects, but reduce temperature control efficiency. Diameters between 25 mm — 80 mm were considered. The optimisation problem followed an iterative approach, where various combinations of D_t, d_p, ϵ, N and P and the Ergun constant calculated to evaluate the feasibility of the design. The procedure was also conducted using the Python library `scipy.optimize` to verify the validity of the trial and error procedure, the code and algorithm for which is included in AppendixA.2.

The results from the optimisation procedure are depicted in Table 5. These parameters

were used to simulate a reactor that was large enough to reach equilibrium. The results were then used to size the reactor to obtain the desirable conversions without diminishing returns.

Table 5: Parameters Used for Pressure Drop Calculation

Parameter	Symbol		Value	Units
Dynamic Viscosity	μ		2.56e-5	$\mathrm{Pa\,s}$
Inlet Gas Density	ρ_0		0.624	$\mathrm{kg\,m^{-3}}$
Inlet Temperature	T_0		723	K
Porosity	ϵ		0.8	-
Catalyst Particle Diameter	d_p		0.006	m
Tube diameter	D_t		0.08	m
Inlet Pressure	P_0		400000	Pa
Bed Density	ρ_B		471	$\mathrm{kg\,m^{-3}}$
Catalyst Density	ρ_c		2355.2	$\mathrm{kg\,m^{-3}}$
Ergun constant	K_w		-9841.5	$\mathrm{Pa\,kg^{-1}}$

Table 6: Additional parameters used in the Energy Balance Calculation

Parameter	Value	Units
$C_{p,\mathrm{CO_2}}$	Dynamically calculated - CoolProp	$\mathrm{J\,mol^{-1}\,K^{-1}}$
$C_{p,\mathrm{CO}}$	Dynamically calculated - CoolProp	$\mathrm{J\,mol^{-1}\,K^{-1}}$
$C_{p,\mathrm{H_2}}$	Dynamically calculated - CoolProp	$\mathrm{J\,mol^{-1}\,K^{-1}}$
$C_{p,\mathrm{H_2O}}$	Dynamically calculated - CoolProp	$\mathrm{J\,mol^{-1}\,K^{-1}}$
$C_{p,\mathrm{CH_4}}$	Dynamically calculated - CoolProp	$\mathrm{J\,mol^{-1}\,K^{-1}}$
Reference Temperature (T_{ref})	298	K
$\Delta H_{\mathrm{Rx_1,298}}$	164.9×10^3	$\mathrm{J\,mol^{-1}}$
$\Delta H_{\mathrm{Rx_2,298}}$	206.3×10^3	$\mathrm{J\,mol^{-1}}$
$\Delta H_{\mathrm{Rx_3,298}}$	-41.1×10^3	$\mathrm{J\,mol^{-1}}$
Stefan-Boltzmann Constant (σ)	5.670×10^{-8}	$\mathrm{W\,m^{-2}\,K^{-4}}$
Absorptivity for Polished Aluminum Steel	0.22	-
Utility Temperature (T_u)	2200	K
Catalyst Particle Diameter (d_p)	0.006	m
Tube diameter (D_t)	0.08	m
Bed Density (ρ_B)	471	$\mathrm{kg\,m^{-3}}$

All of the molar flow rates of reacting species reach a plateau with approximately $8\,\mathrm{kg}$ catalyst, as seen in Figure 3. The conversion of CO_2 effectively plateaus at approximately

87%, with 6 kg of catalyst as seen in Figure 4. The pressure drop, shown in Figure 5, becomes significantly steeper with higher catalyst mass. Large pressure drops increase the energy requirements of the process, which increases the operating costs.
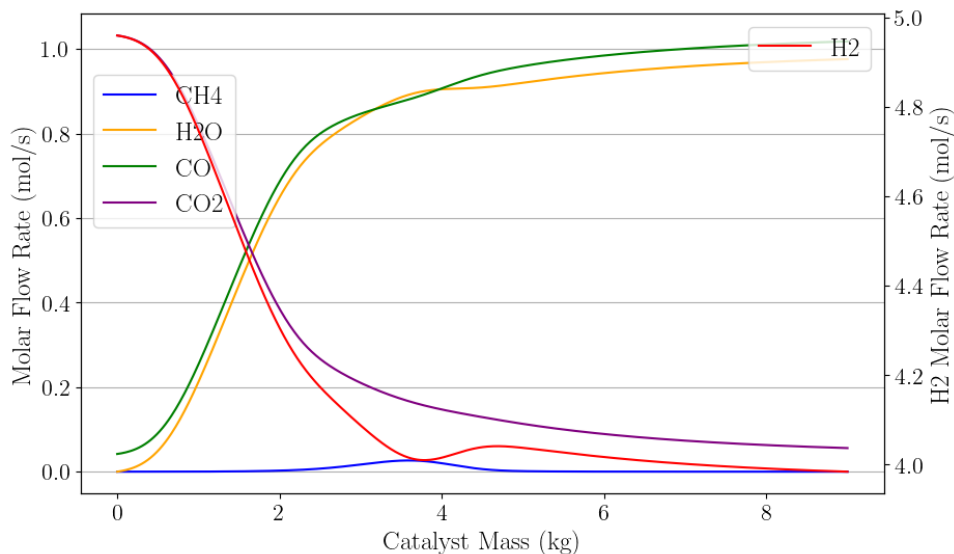

Figure 3: Dual axis plot of the species molar flow rate over the catalyst mass within a single tube of the reactor. CH_4, CO_2, H_2O and CO are plotted on the primary y-axis (Left hand side), and H_2 is plotted on the secondary y-axis (RHS).

The temperature profile, Figure 6, shows that the temperature of the reactor will tend toward the utility temperature. The temperature effect on kinetics is favourable, however excessively high temperatures necessitate the use of more expensive materials of consruction, which dimishes the practical implimentation of the design. Furthermore, unecessarily high temperatures are an unjustifiable operation cost incured due to the furnace duty, which can be seen to rise steeply with catalyst mass in Figure 8.
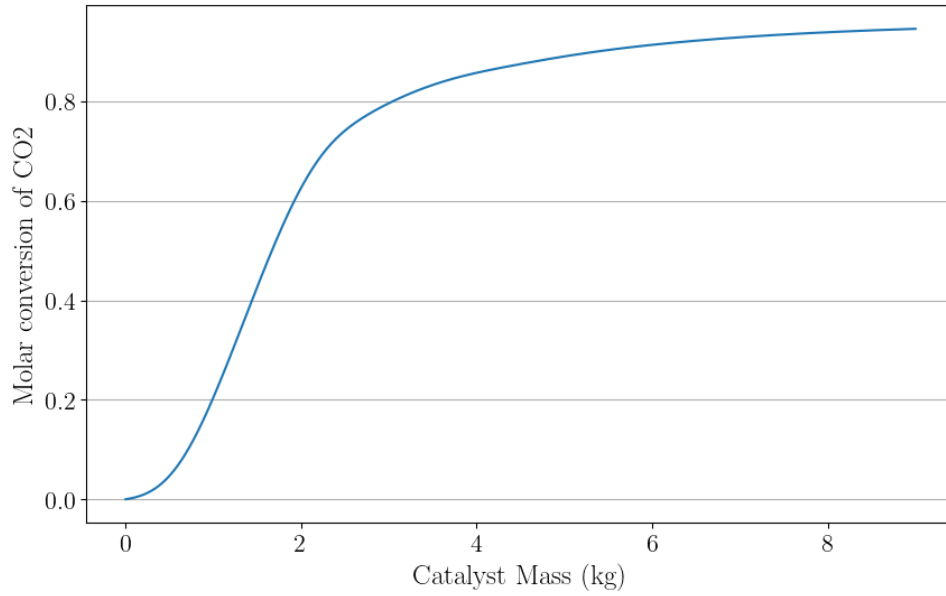
Figure 4: Total conversion of CO_2 over the catalyst mass of the reactor.

A catalyst mass of 3 kg is the point at which the gain of having more catalyst dimishes. Relative to a mass of 8 kg of catalyst, at 3 kg of catalyst the conversion of CO_2 is approximately 6 % lower, the pressure drop is approximately a 75% lower, the outlet temperature is sufficiently high, the furnace duty is 30% less and methane formation is effectively negligeable.
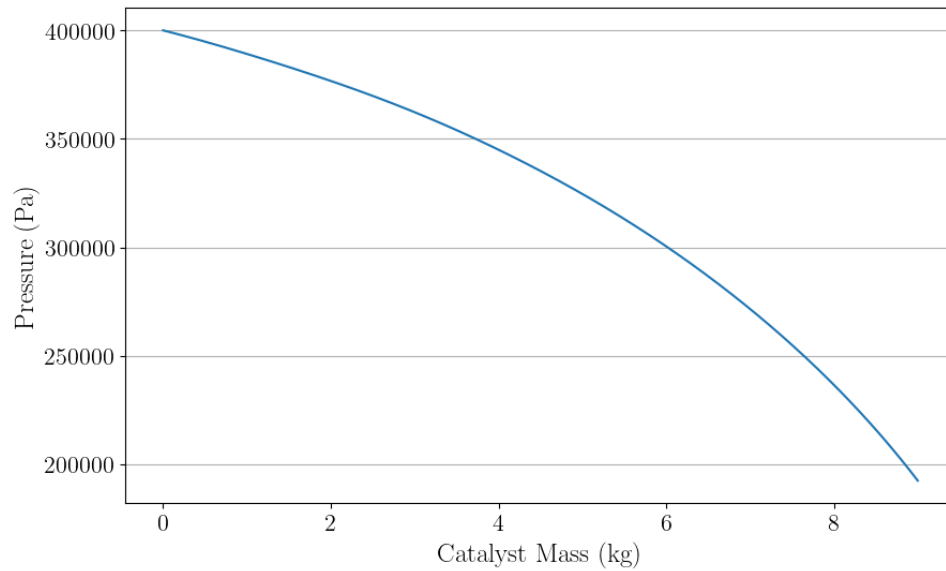

Figure 5: Total pressure drop over the catalyst mass of the reactor.
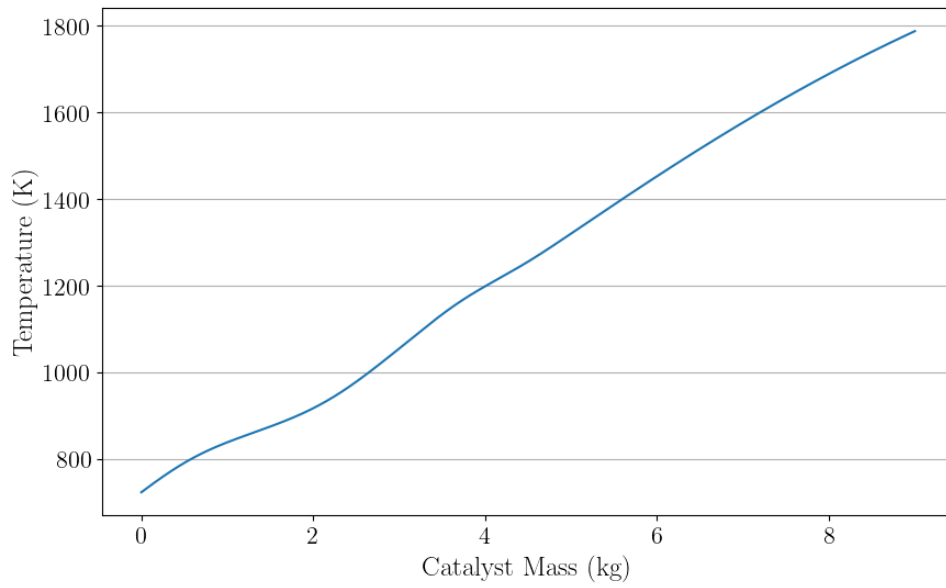
Figure 6: Temperature over the catalyst mass within a single tube of the reactor.
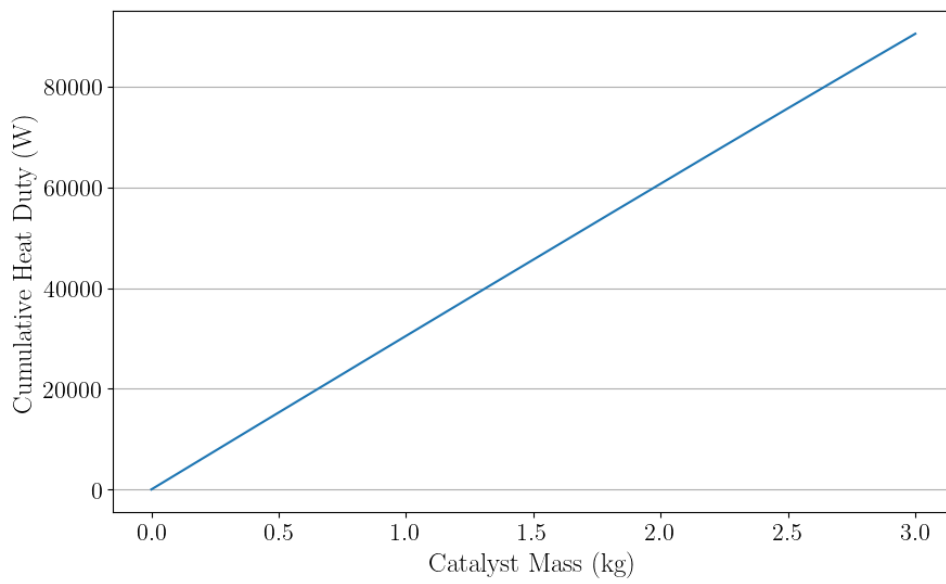

Figure 7: Cumulative heat duty over the catalyst mass of a single tube within the reactor.
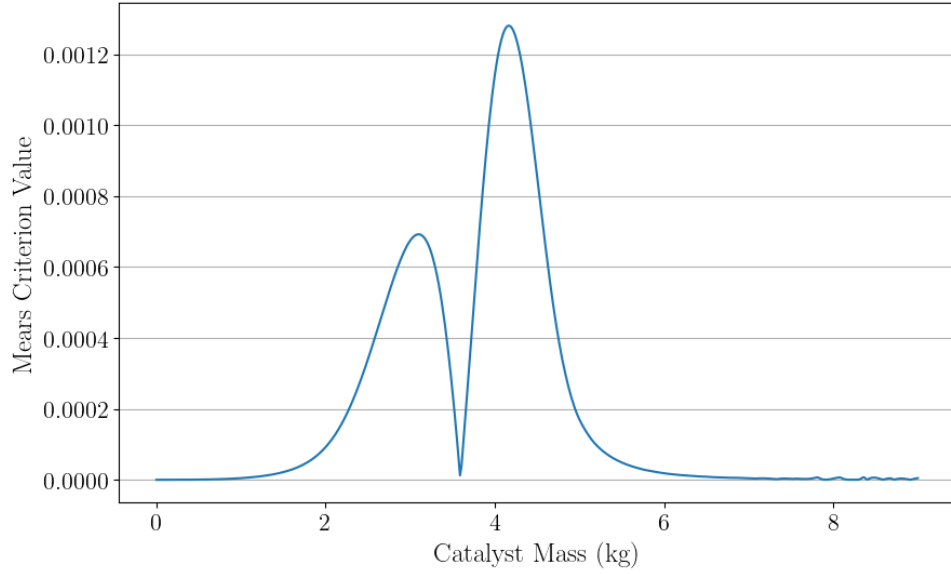
Figure 8: Mears number over the catalyst mass within a single tube of the reactor. Note that this value is well below 0.15, which indicates that the reaction rate is not limited by external mass transfer effects.

3.2 Final design solution

The profiles for the final design are included in this section. The parameters in Table 5 and Table 6 are still relevant, but the total catalyst mass has been reduced from 9000 kg in total to 3000 kg in total.
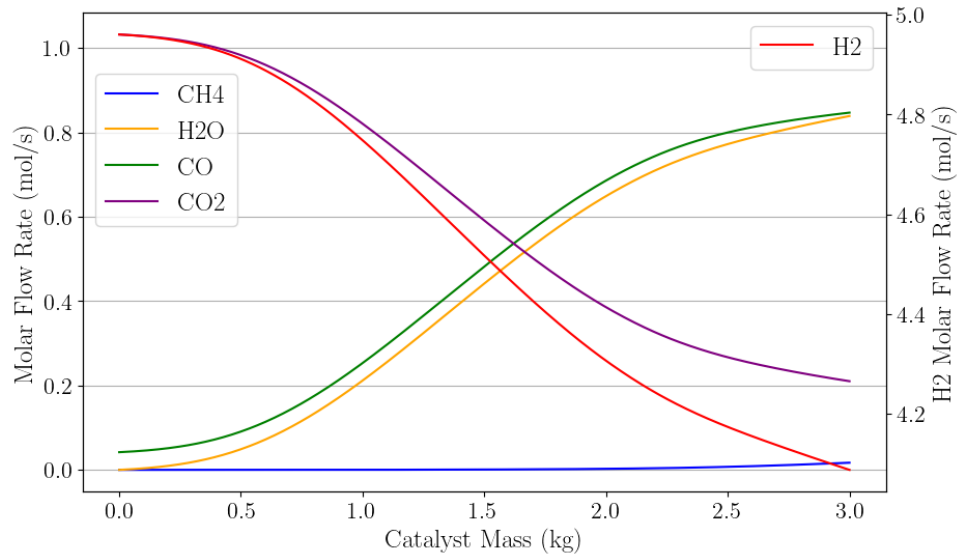
Figure 9: Dual axis plot of the species molar flow rate over the catalyst mass within a single tube of the reactor. CH_4, CO_2, H_2O and CO are plotted on the primary y-axis (Left hand side), and H_2 is plotted on the secondary y-axis (RHS).

15
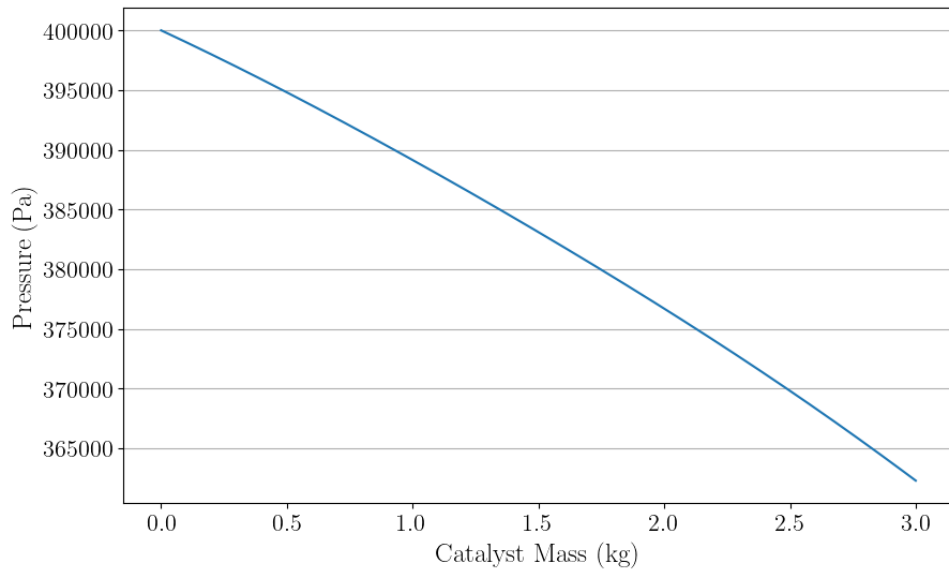
Figure 10: Total pressure drop over the catalyst mass of the reactor

Figure 11: Temperature over the catalyst mass within a single tube of the reactor.

16

Figure 12: Mears number over the catalyst mass within a single tube of the reactor.

Figure 13: Heat duty provided by the furnace to a single tube within the reactor, over the catalyst mass of the tube.
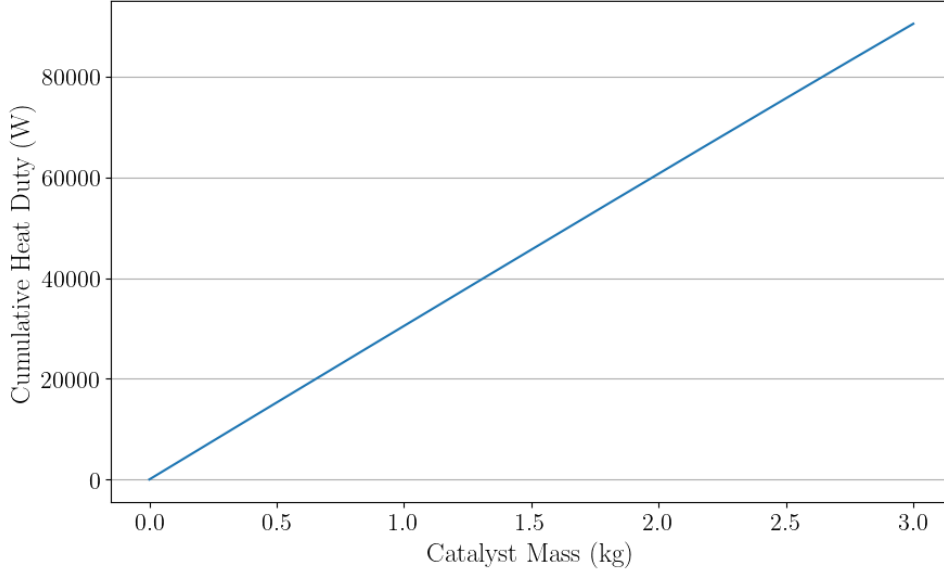
Figure 14: Cumulative heat duty over the catalyst mass of a single tube within the reactor.

4   Physical design

In designing the furnace for the multi-tubular packed bed RWGS reactor, the objective was to achieve uniform heat transfer while maintaining access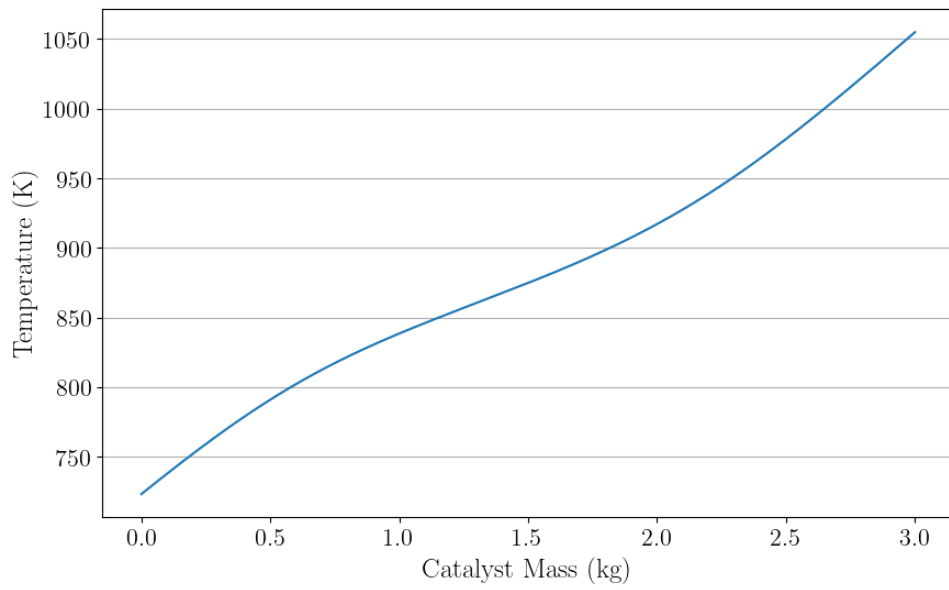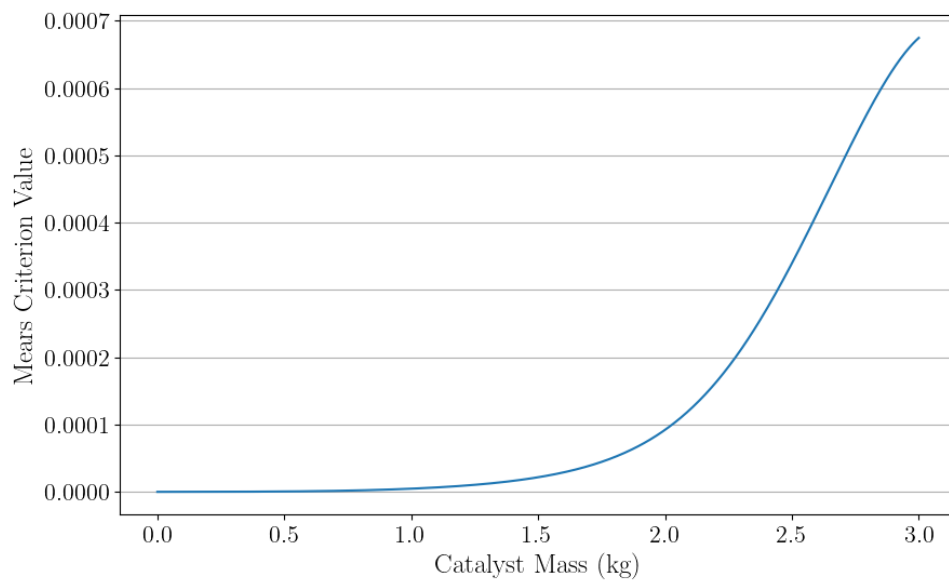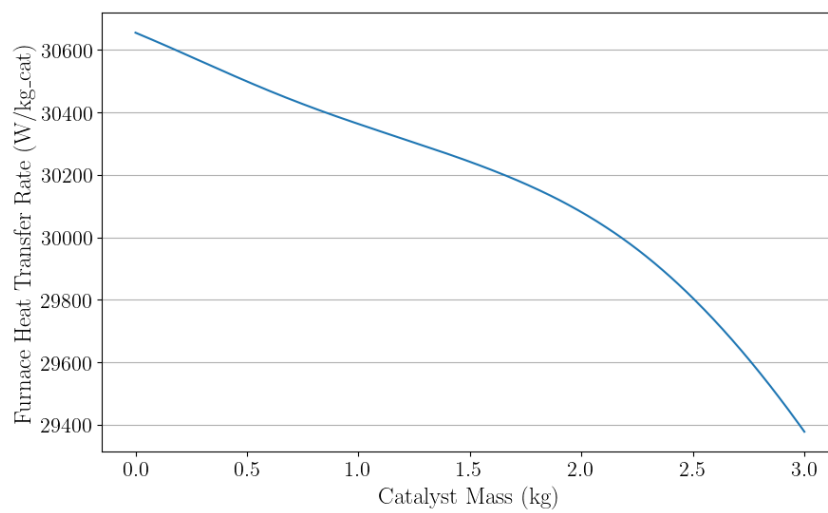ibility for maintenance and inspection. To provide efficient heating within the radiative heat transfer zone, the reactor tubes were designed to be shorter. This design choice improves the absorption of radiant heat.

The tube pitch was set at 1.5 times the tube diameter, resulting in a pitch of 120 mm. This spacing provides clearance between tubes to for heat transfer and provides space for maintenance activities. The number of tubes per row was selected to obtain a rectangular furnace layout, and the tubes were placed in a staggered arrangement, using the calculated pitch for spacing.

The furnace width and depth were calculated using Equations 51 and 52, respectively, which consider the tube pitch and the number of tubes per row to determine the necessary dimensions of the furnace to accommodate all of the tubes. The furnace height was calculated by adding a 1 meter clearance to the reactor tube length, providing space for supports, thermal expansion, and ease of access.

$$W = (N_{\text{row}} - 1) \times P + D_o \tag{51}$$

$$D = (N_{\text{rows}} - 1) \times P_{\text{eff}} + D_o \tag{52}$$

18

The number of burners required was determined by dividing the total heat duty by the heat capacity of each burner. Burners with a capacity of approximately 4.2 MW per burner, as discussed in Oilon Oy, 2023. The final furnace design is included in Table 7, the flow of gasses will enter from the top of the furnace and exit from the bottom. The burners are placed adjacent to each other along sides of tubes firing upwards, thus creating a counter current flow to that of the reacting gasses in the tubes. A drawing of the design is included as Figure 15.

Table 7: Furnace design parameters

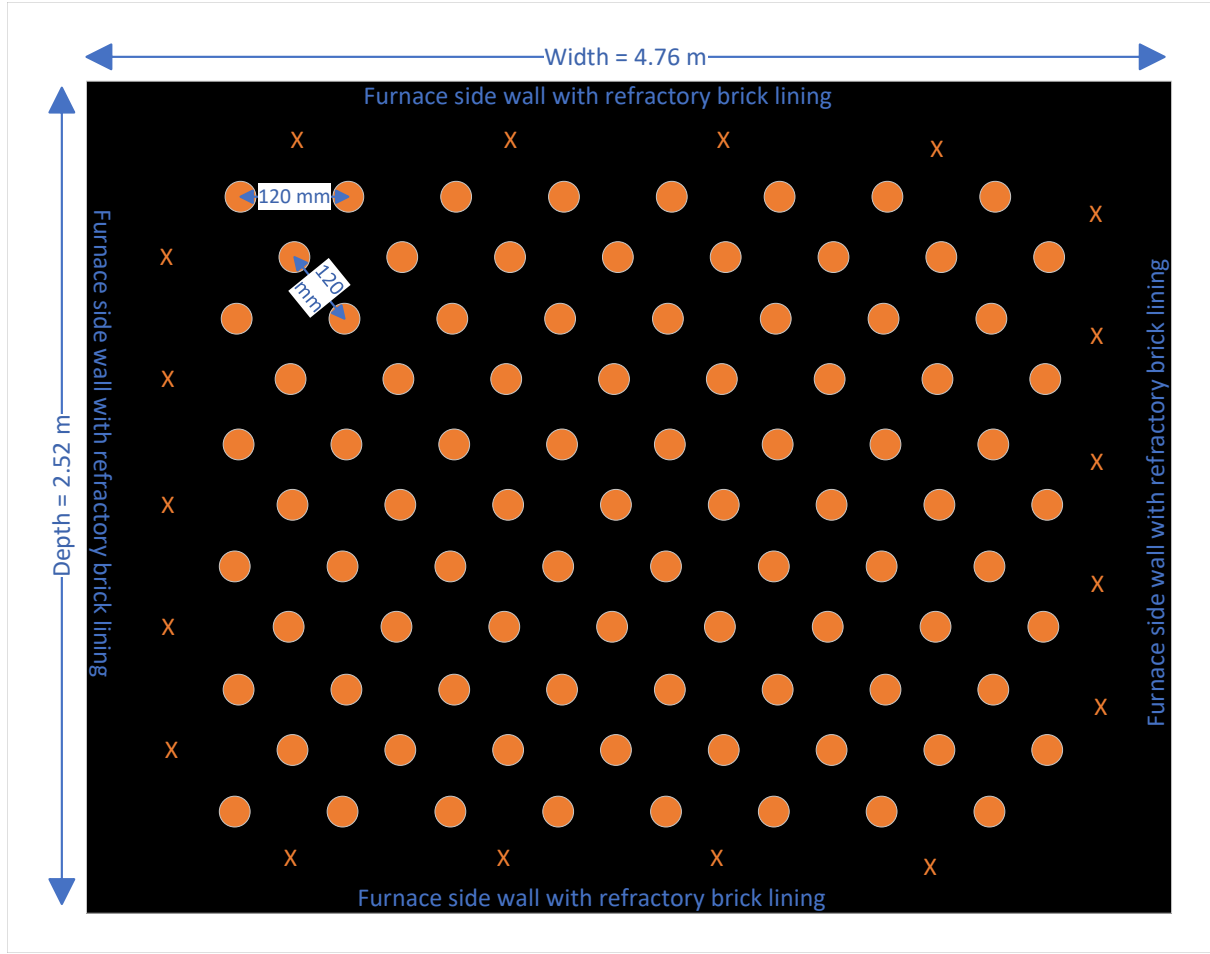| Parameter	Value	Unit
Total number of tubes	1000	-
Tube outside diameter (OD)	80	mm
Tube pitch	120.00	mm
Tube arrangement	Staggered	-
Number of tubes per row	40	-
Number of rows	25	-
Furnace width	4.76	m
Furnace depth	2.57	m
Furnace height	2.27	m
Total heat duty	90.52	MW
Individual burner capacity	4.2	MW
Number of burners required	22	-

Figure 15: Top view of the furnace, depicting tube arrangement and spacing. The orange circles are the reactor tubes and the orange X's are the burners. Note that this figure does not include all of the rows, tubes and burners, but depicts the the spacing and layout of the furnace.

Based on the operating conditions: temperatures up to 1100 K, pressure s up to 400 kPa, high hydrogen content, and exposure to a gas-fired furnace environment. Inconel 601 (UNS N06601) would be a suitable material for the tubes. This material has high-temperature strength, oxidation resistance, and resistance to Hydrogen embrittlement at elevated temperatures Green and Southard, 2019. Reactor tube thickness of 4 mm was selected, and a nominal pipe diameter of 80 mm (Greeff and Skinner, 2000).

The size of the pipes entering and leaving the reactor were sized based on the recommended linear velocities for gas Greeff and Skinner, 2000, to be between $5 \, \mathrm{m \, s^{-1}}$ and $100 \, \mathrm{m \, s^{-1}}$. The total mass flow rate of material into the reactor is $56.6 \, \mathrm{kg \, s^{-1}}$ at a density of $0.624 \, \mathrm{kg \, m^{-3}}$. Thus, a pipe diameter of 1.1 m is required to result in an outlet linear velocity of $92.8 \, \mathrm{m \, s^{-1}}$. The mass flow rate out of the reactor is the same and the gas density is $0.39 \, \mathrm{kg \, m^{-3}}$. Thus, a pipe diameter of 1.4 m is required to result in an outlet linear velocity of $94.28 \, \mathrm{m \, s^{-1}}$. The piping was selected based on the calculated required

diameter for recommended gas linear velocities and standard piping sizes.

The pipe sizing for entering and exiting streams are as follows. A nominal pipe diameter of 1.2 m has an outside diameter of 1.22 m, large enough for the entering stream with allowance for thickness requirements. Similarly, a nominal pipe diameter of 1.400 m has an outside diameter of 1.42 m, large enough for the exiting stream with allowance for thickness requirements.

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A Appendix

A.1 Appendix A1

This appendix contains the python code used to simulate the kinetics, mass transfer, pressure drop and energy balance over the reactor.

```python
# Reactor specs
N = 1000 # number of tubes
Dt = 0.08 # m  between 25 to 75 mm # ! mass flux is huge, so we need to
    show how Kw varies with Dt,

# Bed specs
por = 0.8 # m^3 void / m^3 bed
rhoc = 2355.2 # kg/m^3
rhoB = rhoc * (1 - por) # kg cat / m^3 bed
dp = 0.006 # m
Ac = np.pi * Dt**2 / 4 # m^2, cross sec area of 1 tube

# Constants and reactor conditions
R = 8.314  # Gas constant, J/(mol*K)
P0 = 4 *100*1000  # Pressure in bar (example)
T0 = 450 + 273.15  # Temperature in Kelvin
W_max = 3000/N  # Total catalyst mass in kg, per reactor tube
L = W_max /(Ac * rhoB) # m
L

# !Stoichiometric coefficients for the reactions
# Steam reforming: CH4 + H2O <-> CO + 3H2 delH = 206.3 kJ/mol
nu_steam_reforming = {'CH4': -1, 'H2O': -1, 'CO': 1, 'H2': 3}

# Methanation: CH4 + 2H2O <-> CO2 + 4H2 delH = 164.9 kJ/mol
nu_methanation = {'CH4': -1, 'H2O': -2, 'CO2': 1, 'H2': 4}

# WGS: CO + H2O <-> CO2 + H2  delH = -41.1 kJ/mol
nu_rwgs = {'CO': -1, 'H2O': -1, 'CO2': 1, 'H2': 1}
```

```python
30  # !Energy balance
31  # Heat capacities
32  Cp_CO2 = PropsSI('CPMOLAR', 'T', T0, 'P', P0, 'CO2')  # J/mol.K
33  Cp_CO = PropsSI('CPMOLAR', 'T', T0, 'P', P0, 'CO') # J/mol.K
34  Cp_H2 = PropsSI('CPMOLAR', 'T', T0, 'P', P0, 'H2') # J/mol.K
35  Cp_H2O = PropsSI('CPMOLAR', 'T', T0, 'P', P0, 'H2O') # J/mol.K
36  Cp_CH4 = PropsSI('CPMOLAR', 'T', T0, 'P', P0, 'CH4') # J/mol.K
37  # Heats of reaction at Tref
38  T_ref = 298 # K
39  delH_Rx_1_298 = 164.9 * 1000 # J/mol.K
40  delH_Rx_2_298 = 206.3 * 1000 # J/mol.K
41  delH_Rx_3_298 = -41.1 * 1000 # J/mol.K
42  # Boltzman constant
43  Boltz_con = 5.67 * 10**(-8) # J/(s.m^2.K^4)
44  # Absorptivity for polished aluminim steel for a radiative source at
    ↪   2200K
45  absorptivity = 0.22
46  # Utility Temp, adiabatic flam temp of hydrocarbon
47  Tu = 2200 # K
```

```python
1       # Feed- initial conditions, note #! WE MODEL BY 1 TUBE
2  # Initial molar flow rates (mol/s)
3  # F_N2 = 0.1974732 * 1000
4  F0_CO2 = (0.52255 * 1000 + 0.50966735 * 1000) / N
5  F0_CO = (0.041902342 * 1000) / N
6  F0_H2 = (4.960612735 * 1000) / N
7  F0_H2O = 0 / N
8  F0_CH4 = 0 / N
9  F0_t = F0_CO2 + F0_CO + F0_H2 + F0_H2O + F0_CH4
10
11  # molar mass
12  MM_CO2 = 44.01 / 1000 # kg/mol
13  MM_CO = 28.01 / 1000 # kg/mol
14  MM_H2 = 2.016 / 1000 # kg/mol
15  MM_H2O = 18.01528 / 1000 # kg/mol
16  MM_CH4 = 16.04 / 1000 # kg/mol
17
```

A.2

```python
18  # mass flows per tube
19  M0_CO2 = F0_CO2 * MM_CO2 # kg/s
20  M0_CO = F0_CO * MM_CO # kg/s
21  M0_H2 = F0_H2 * MM_H2 # kg/s
22  M0_H2O = F0_H2O * MM_H2O # kg/s
23  M0_CH4 = F0_CH4 * MM_CH4 # kg/s
24  M_total = M0_CO2 + M0_CO + M0_H2 + M0_H2O + M0_CH4 # kg/s, of one tube
    ↪  !!
25
26  # Molar fractions of each component
27  y0_CO2 = F0_CO2 / F0_t
28  y0_CO = F0_CO / F0_t
29  y0_H2 = F0_H2 / F0_t
30  y0_H2O = F0_H2O / F0_t
31  y0_CH4 = F0_CH4 / F0_t
32  MM_avg = y0_CO2 * MM_CO2 + y0_CO * MM_CO + y0_H2 * MM_H2 + y0_H2O *
    ↪  MM_H2O + y0_CH4 * MM_CH4
33
34  # Calculate Ergun CONSTANT
35  G = M_total / Ac # kg/(m^2.s.tube), mass flux through a single tube
36  mu_0 = 2.5623*10**(-5) # pa.s coolprop at 1023 K and 2 bar
37  # rho_0 = 0.617547 # kg/m^3 from DWSIM at
38  rho_0 = MM_avg * P0 / (R * T0) # kg / m^3
39  KW = -G/(Ac * rho_0 * rhoB * dp) * ((1 - por) / por**3) * (150 * mu_0 *
    ↪  (1 - por) / dp + 1.75 * G)
40  KW
41  # M_total*N
42
43  # Internal mass transfer, from Rahimpour, we will prorate later
44  dp_old = 0.005 # m Fromet de Groote
45  T_eff_ref = 900 + 273.15 # K, Fromet de Groote
46  # Prorated to my cat diameter
47  eff1o = 0.07 * dp_old / dp
48  eff2o = 0.06 * dp_old / dp
49  eff3o = 0.7 * dp_old / dp
50
51  # Diffusivity of CO2 at reference temp 273 K
52  D_CO2_mix_273 = 2.17*10**-5 #  m^2/s
```

```python
# Define the Arrhenius equation for rate constants
def arrhenius_eq(k0, Ea, T):
    return k0 * np.exp(-Ea / (R * T))

# Define Van't Hoff to solve for adsorption coefficient
def Adsorption(Koi, dH_i, T):
    return Koi * np.exp(-dH_i / (R * T))

def calculate_mears_criterion(r_prime, dp, P_A_bulk, rho, mu, D_AB, u,
    T):
    """
    Calculate Mears Criterion to evaluate external mass transfer
        limitations.

    Parameters:
    r_prime : float
        Reaction rate per unit volume of catalyst particle
            [mol/(m^3·s)]
    dpp : float
        Catalyst particle diameter [m]
    P_A_bulk : float
        Bulk partial pressure of reactant A [mol/m^3]
    rho : float
        Gas density [kg/m^3]
    mu : float
        Gas viscosity [Pa·s]
    D_AB : float
        Diffusivity of A in bulk gas mixture [m^2/s]
    u : float
        Superficial gas velocity [m/s]
    """

    # Calculate Reynolds number
    Re = (rho * u * dp) / mu

    # Calculate Schmidt number
    Sc = mu / (rho * D_AB)

```

```python
36        # Calculate Sherwood number using Ranz-Marshall correlation
37        Sh = 2 + 0.6 * (Re**0.5) * Sc**(1/3)
38
39        # Calculate mass transfer coefficient
40        k_c = (Sh * D_AB) / dp
41
42        # Calculate Mears criterion
43        mears_criterion_value = (r_prime * dp * 0.5 * R * T) / (P_A_bulk *
       ↪   k_c)
44
45        return Re, Sc, Sh, k_c, mears_criterion_value
46
47
48
49   Q_values = []
50   mears_values  = []
51   # Define the reaction rates
52   def reaction_rates(F_CH4, F_H2, F_H2O, F_CO, F_CO2, P, T, W):
53        # Total molar flow rate (mol/s)
54        F_total = F_CH4 + F_H2 + F_H2O + F_CO + F_CO2
55
56        # Calculate partial pressures (assuming ideal gas)
57        P_CH4 = P * F_CH4 / F_total
58        P_H2 = P * F_H2 / F_total
59        P_H2O = P * F_H2O / F_total
60        P_CO = P * F_CO / F_total
61        P_CO2 = P * F_CO2 / F_total
62
63        # Arrhenius parameters for each reaction
64        k0_1, Ea_1 = 1.17e15 * (10**5)**0.5, 240100  # Methanation
65        k0_2, Ea_2 = 2.83e14 * (10**5)**0.5, 243900  # Steam reforming
66        k0_3, Ea_3 = 5.43e5 / (10**5), 67130     # Reverse Water-Gas Shift
67        # print('k')
68        # print(k0_1, k0_2, k0_3)
69        # print('Ea')
70        # print(Ea_1, Ea_2, Ea_3)
71        # Equilibrium constants (as functions of T) original eqns in bar^2
72        K1 = np.exp(-26830 / T + 30.114) * 10**10
73        K2 = K1 * np.exp(4400 / T - 4.036)
```

```python
74    K3 = np.exp(4400 / T - 4.036)
75    # Rate constants at temperature T
76    k1 = arrhenius_eq(k0_1, Ea_1, T)
77    k2 = arrhenius_eq(k0_2, Ea_2, T)
78    k3 = arrhenius_eq(k0_3, Ea_3, T)
79
80    # Adsorption parameters for Species (delH in J/mol)
81    Ko_CH4, dH_CH4 = 6.65*10**(-4)*10**(-5), -38280   # CH4
82    Ko_CO, dH_CO = 8.23*10**(-5)*10**(-5), -70650   # CO
83    Ko_H2, dH_H2 = 6.12*10**(-9)*10**(-5), -82900     # H2
84    Ko_H2O, dH_CO2 = 1.77*10**(5), 88680      # C2O
85
86    # Adsorption constants
87    K_CH4 = Adsorption(Ko_CH4, dH_CH4, T)
88    K_CO = Adsorption(Ko_CO, dH_CO, T)
89    K_H2 = Adsorption(Ko_H2, dH_H2, T)
90    K_H2O = Adsorption(Ko_H2O, dH_CO2, T)
91    # print('K')
92    # print(Ko_CH4, Ko_CO, Ko_H2, Ko_H2O)
93    # print('dH')
94    # print(dH_CH4, dH_CO, dH_H2, dH_CO2)
95
96    # Internal mass transfer pro rate to temp
97    eff1 = eff1o * np.exp(Ea_1/(2 * R)*(-1/T + 1/T_eff_ref))
98    eff2 = eff2o * np.exp(Ea_2/(2 * R)*(-1/T + 1/T_eff_ref))
99    eff3 = eff3o * np.exp(Ea_3/(2 * R)*(-1/T + 1/T_eff_ref))
100   # eff1 = eff1o * np.exp((-1/T + 1/T_eff_ref))
101   # eff2 = eff2o * np.exp((-1/T + 1/T_eff_ref))
102   # eff3 = eff3o * np.exp((-1/T + 1/T_eff_ref))
103   # Reaction rate expressions
104   DEN = 1 + K_CO * P_CO + K_H2 * P_H2 + K_CH4 * P_CH4 + K_H2O * P_H2O /
      ↪  P_H2
105   r1 = eff1 * k1 / (P_H2)**2.5 * (P_CH4 * P_H2O - P_H2**3 * P_CO / K1)
      ↪  * 1 / DEN**2 # steam methane reforming
106   r2 = eff2 * k2 / (P_H2)**3.5 * (P_CH4 * P_H2O**2 - P_H2**4 * P_CO2 /
      ↪  K2) * 1 / DEN**2 # Methanation
107   r3 = eff3 * k3 / (P_H2) * (P_CO * P_H2O - P_H2 * P_CO2 / K3) * 1 /
      ↪  DEN**2 # RWGS
108
```

A.6

```python
109        # Check for external mass transfer using mears criterion
110        # global mears_values
111        # Molar fractions of each component
112        y_CO2 = F_CO2 / F_total
113        y_CO = F_CO / F_total
114        y_H2 = F_H2 / F_total
115        y_H2O = F_H2O / F_total
116        y_CH4 = F_CH4 / F_total
117        MM_avg = y_CO2 * MM_CO2 + y_CO * MM_CO + y_H2 * MM_H2 + y_H2O *
           ↪  MM_H2O + y_CH4 * MM_CH4
118        rho_mears = MM_avg * P / (R * T)
119        u = (F_total * R * T / P) / Ac
120        D_CO2_mix_T = D_CO2_mix_273 * T0 * (T / 273)**(3/2) * (101325 / P) #
           ↪  prorate the diffusivity based on T and P
121        mears_value = calculate_mears_criterion(abs(r1 * rhoB), dp, P_CO2,
           ↪  rho_mears, mu_0, D_CO2_mix_T, u, T)[4]
122        # Check if W is close to one of the evaluation points
123        # Store mears_value at evaluation points
124        # tolerance = 1e-6
125        # if np.any(np.abs(W - W_eval) < tolerance):
126        #     mears_values.append(mears_value)
127        # else:
128        #     pass
129        return r1, r2, r3
130
131
132    # ODEs for mole balances in the packed bed reactor
133    def mole_balances(W, var):
134        F_CH4, F_H2, F_H2O, F_CO, F_CO2, P, T = var
135        F_t = F_CH4 + F_H2 + F_H2O + F_CO + F_CO2
136        # Get reaction rates
137        r1, r2, r3 = reaction_rates(F_CH4, F_H2, F_H2O, F_CO, F_CO2, P, T, W)
138
139        # Stoichiometric coefficients for each species #! Put in
           ↪  effectiveness here later according to R paper
140        dF_CH4_dW =  nu_steam_reforming['CH4'] * r1 +  nu_methanation['CH4']
           ↪  * r2
141        dF_H2_dW =  nu_steam_reforming['H2'] * r1 +  nu_methanation['H2'] *
           ↪  r2 + nu_rwgs['H2'] * r3
```

A.7

```python
142    dF_H2O_dW =  nu_steam_reforming['H2O'] * r1 +  nu_methanation['H2O']
       ↪    * r2 + nu_rwgs['H2O'] * r3
143    dF_CO_dW =  nu_steam_reforming['CO'] * r1 +  nu_rwgs['CO'] * r3
144    dF_CO2_dW =  nu_methanation['CO2'] * r2 +  nu_rwgs['CO2'] * r3
145
146    # Ergun
147    dP_dW = KW * (P0 * F_t * T / (P * F0_t  * T0))
148
149    # !Energy balance
150    # Calc change in Cprxn, note that i am assuming Cp stays the same
151    delCprx1 = nu_steam_reforming['CH4']*Cp_CH4 +
       ↪   nu_steam_reforming['H2O']*Cp_H2O + nu_steam_reforming['CO']*Cp_CO
       ↪   + nu_steam_reforming['H2']*Cp_H2
152    delCprx2 = nu_methanation['CH4']*Cp_CH4 +
       ↪   nu_methanation['H2O']*Cp_H2O + nu_methanation['CO2']*Cp_CO2 +
       ↪   nu_methanation['H2']*Cp_H2
153    delCprx3 = nu_rwgs['CO']*Cp_CO + nu_rwgs['H2O']*Cp_H2O +
       ↪   nu_rwgs['CO2']*Cp_CO2 + nu_rwgs['H2']*Cp_H2
154    # Calc delHrxn
155    delHrx1      = delH_Rx_1_298 + delCprx1*(T - T_ref)
156    delHrx2      = delH_Rx_2_298 + delCprx2*(T - T_ref)
157    delHrx3      = delH_Rx_3_298 + delCprx3*(T - T_ref)
158    ri_vi_delHrx= delHrx1*(r1) + delHrx2*(r2) + delHrx3*(r3) # Note that
       ↪   ri is already per mol rxn, so no need for denominator stoic
159
160    sum_Fi_Cpi  = F_CH4 * Cp_CH4 + F_H2 * Cp_H2 + F_H2O * Cp_H2O + F_CO *
       ↪   Cp_CO + F_CO2 * Cp_CO2
161    Q = absorptivity * Boltz_con * (Tu**4 - T**4) * 4 / (Dt * rhoB) #
       ↪   W/kgcat, non adiabatic term U*a*(T_u - T)
162    dT_dW       = (Q - ri_vi_delHrx) / sum_Fi_Cpi
163
164    # global Q_values
165    # # Append Q at evaluation points
166    # tolerance = 1e-6
167    # if np.any(np.abs(W - W_eval) < tolerance):
168    #     Q_values.append(Q)
169    # else:
170    #     pass
```

```
171     return [dF_CH4_dW, dF_H2_dW, dF_H2O_dW, dF_CO_dW, dF_CO2_dW, dP_dW,
        ↪   dT_dW]

172

173 var0 = [F0_CH4, F0_H2, F0_H2O, F0_CO, F0_CO2, P0, T0]   # Initial values
    ↪   for CH4, H2, H2O, CO, CO2

174

175 # Solve the ODEs using solve_ivp with t_eval

176

177 W_eval = np.linspace(0, W_max, num=500)
178 solution = solve_ivp(mole_balances, [0, W_max], var0, method='Radau',
    ↪   t_eval=W_eval)

179

180

181 # Plot the results

182

183 # Primary y-axis for CH4, H2O, CO, CO2
184 fig, ax1 = plt.subplots()
185 ax1.plot(solution.t, solution.y[0], label='CH4', color='blue')
186 ax1.plot(solution.t, solution.y[2], label='H2O', color='orange')
187 ax1.plot(solution.t, solution.y[3], label='CO', color='green')
188 ax1.plot(solution.t, solution.y[4], label='CO2', color='purple')
189 ax1.set_xlabel('Catalyst Mass (kg)')
190 ax1.set_ylabel('Molar Flow Rate (mol/s)')
191 ax1.legend(loc='upper left', bbox_to_anchor=(0, 0.9))
192 # Enable horizontal grid lines only
193 ax1.yaxis.grid(True)
194 ax1.xaxis.grid(False)
195 # ax1.set_title('Molar Flow Rates in Packed Bed Reactor')

196

197 # Create secondary y-axis for H2 data
198 ax2 = ax1.twinx()
199 ax2.plot(solution.t, solution.y[1], label='H2', color='red')
200 ax2.set_ylabel('H2 Molar Flow Rate (mol/s)', color='k')
201 ax2.tick_params(axis='y', labelcolor='k')
202 ax2.legend(loc='upper right', bbox_to_anchor=(1, 1.0))

203

204 # Show the plot
205 plt.show()

206
```

```
207  # Print reactor length
208  print(f'Reactor length = {L}m')
209  \end{lstlisting}
210
211  \begin{lstlisting}[language=Python, caption={Python code for reactor
     ↪  simulation, part 4}]
212      # Solve the ODEs using solve_ivp
213  desired_number_of_points = 500  # Adjust as needed
214  W_eval = np.linspace(0, W_max, num=desired_number_of_points)
215  solution = solve_ivp(mole_balances, [0, W_max], var0, method='Radau',
     ↪  t_eval=W_eval)
216
217  # Initialize lists to store Q and mears values
218  Q_values = []
219  mears_values = []
220
221  # Loop over the solution points to compute Q and mears
222  for i in range(len(solution.t)):
223      W = solution.t[i]
224      F_CH4, F_H2, F_H2O, F_CO, F_CO2, P, T = solution.y[:, i]
225
226      # Total molar flow rate (mol/s)
227      F_total = F_CH4 + F_H2 + F_H2O + F_CO + F_CO2
228
229      # Calculate partial pressures (assuming ideal gas)
230      P_CH4 = P * F_CH4 / F_total
231      P_H2 = P * F_H2 / F_total
232      P_H2O = P * F_H2O / F_total
233      P_CO = P * F_CO / F_total
234      P_CO2 = P * F_CO2 / F_total
235
236      # Compute reaction rates
237      r1, r2, r3 = reaction_rates(F_CH4, F_H2, F_H2O, F_CO, F_CO2, P, T, W)
238
239      # Compute Q
240      # Recompute necessary variables for Q
241      delCprx1 = nu_steam_reforming['CH4']*Cp_CH4 +
         ↪  nu_steam_reforming['H2O']*Cp_H2O + nu_steam_reforming['CO']*Cp_CO
         ↪  + nu_steam_reforming['H2']*Cp_H2
```

A.10

```
242    delCprx2 = nu_methanation['CH4']*Cp_CH4 +
  ↪    nu_methanation['H2O']*Cp_H2O + nu_methanation['CO2']*Cp_CO2 +
  ↪    nu_methanation['H2']*Cp_H2
243    delCprx3 = nu_rwgs['CO']*Cp_CO + nu_rwgs['H2O']*Cp_H2O +
  ↪    nu_rwgs['CO2']*Cp_CO2 + nu_rwgs['H2']*Cp_H2
244    # Calc delHrxn
245    delHrx1 = delH_Rx_1_298 + delCprx1*(T - T_ref)
246    delHrx2 = delH_Rx_2_298 + delCprx2*(T - T_ref)
247    delHrx3 = delH_Rx_3_298 + delCprx3*(T - T_ref)
248    ri_vi_delHrx = delHrx1*(r1) + delHrx2*(r2) + delHrx3*(r3)
249    sum_Fi_Cpi = F_CH4 * Cp_CH4 + F_H2 * Cp_H2 + F_H2O * Cp_H2O + F_CO *
  ↪    Cp_CO + F_CO2 * Cp_CO2
250    Q = absorptivity * Boltz_con * (Tu**4 - T**4) * 4 / (Dt * rhoB)
251    Q_values.append(Q)
252
253    # Compute Mears Criterion
254    # Molar fractions
255    y_CO2 = F_CO2 / F_total
256    y_CO = F_CO / F_total
257    y_H2 = F_H2 / F_total
258    y_H2O = F_H2O / F_total
259    y_CH4 = F_CH4 / F_total
260    MM_avg = y_CO2 * MM_CO2 + y_CO * MM_CO + y_H2 * MM_H2 + y_H2O *
  ↪    MM_H2O + y_CH4 * MM_CH4
261    rho_mears = MM_avg * P / (R * T)
262    u = (F_total * R * T / P) / Ac
263    D_CO2_mix_T = D_CO2_mix_273 * T0 * (T / 273)**(3/2) * (101325 / P)
264    r_prime = abs(r1 * rhoB)
265    Re, Sc, Sh, k_c, mears_value = calculate_mears_criterion(r_prime, dp,
  ↪    P_CO2, rho_mears, mu_0, D_CO2_mix_T, u, T)
266    mears_values.append(mears_value)
267
268 # Now, Q_values and mears_values have the same length as solution.t
```

A.2 Appendix A2

This appendix contains includes the Python code used for the optimisation:

```python
L_min = 0.01   # m (minimum reactor length)
L_max = 8      # m (maximum reactor length)
W = 5000

def objective_function(x):
    Dt, P0, por, N, dp = x
    F0_CO2 = (0.52255 * 1000 + 0.50966735 * 1000) / N
    F0_CO = (0.041902342 * 1000) / N
    F0_H2 = (4.960612735 * 1000) / N
    F0_H2O = 0 / N
    F0_CH4 = 0 / N
    F0_t = F0_CO2 + F0_CO + F0_H2 + F0_H2O + F0_CH4

    # molar mass
    MM_CO2 = 44.01 / 1000 # kg/mol
    MM_CO = 28.01 / 1000 # kg/mol
    MM_H2 = 2.016 / 1000 # kg/mol
    MM_H2O = 18.01528 / 1000 # kg/mol
    MM_CH4 = 16.04 / 1000 # kg/mol

    # mass flows per tube
    M0_CO2 = F0_CO2 * MM_CO2 # kg/s
    M0_CO = F0_CO * MM_CO # kg/s
    M0_H2 = F0_H2 * MM_H2 # kg/s
    M0_H2O = F0_H2O * MM_H2O # kg/s
    M0_CH4 = F0_CH4 * MM_CH4 # kg/s
    M_total = M0_CO2 + M0_CO + M0_H2 + M0_H2O + M0_CH4 # kg/s, of one
    ↪    tube !!
    Ac = np.pi * Dt**2 / 4 # m^2, cross sec area of 1 tube
    W_max = W/N
    T0 = 450 + 273.15   # K
    G = M_total / Ac # kg/(m^2.s.tube), mass flux through a single tube
    mu_0 = 3.2649*10**(-5) # pa.s coolprop at 1023 K and 2 bar
    # rho_0 = 0.617547 # kg/m^3 from DWSIM at
    rho_0 = MM_avg * P0 / (R * T0) # kg / m^3
    rhoB = rhoc * (1 - por)
    KW = -G/(Ac * rho_0 * rhoB * dp) * ((1 - por) / por**3) * (150 * mu_0
    ↪    * (1 - por) / dp + 1.75 * G)
```

A.12

```python
37      return KW
38
39  def reactor_length_upper_constraint(x):
40      Dt, P0, por, N, dp = x
41      Ac = np.pi * Dt**2 / 4
42      rhoB = rhoc * (1 - por)
43      W_max = W / N
44      L = W_max / (Ac * rhoB)
45      return L_max - L   # Must be >= 0
46
47  def reactor_length_lower_constraint(x):
48      Dt, P0, por, N, dp = x
49      Ac = np.pi * Dt**2 / 4
50      rhoB = rhoc * (1 - por)
51      W_max = W / N
52      L = W_max / (Ac * rhoB)
53      return L - L_min   # Must be >= 0
54
55  bounds = Bounds(
56      [0.025, 10**5, 0.4, 200, 0.003],   # Lower bounds
57      [0.08, 8*10**5, 0.8, 1000, 0.006]    # Upper bounds
58  )
59  constraints = [
60      {'type': 'ineq', 'fun': reactor_length_upper_constraint},
61      {'type': 'ineq', 'fun': reactor_length_lower_constraint}
62  ]
63
64  x0 = [0.075, 4*10**5, 0.8, 600, 0.005]
65
66  # Perform optimization
67  result = minimize(
68      objective_function,
69      x0,
70      method='SLSQP',
71      bounds=bounds,
72      constraints=constraints,
73      options={'disp': True}
74  )
75
```

```python
76  # Check if optimization was successful
77  if result.success:
78      Dt_opt, P0_opt, por_opt, N_opt, dp_opt = result.x
79      KW_opt = result.fun
80
81      # Recalculate reactor length
82      Ac_opt = np.pi * Dt_opt**2 / 4
83      rho_B_opt = rhoc * (1 - por_opt)
84      W_max_opt = W / N_opt
85      L_opt = W_max_opt / (Ac_opt * rho_B_opt)
86
87      print(f"Optimal Tube Diameter (Dt): {Dt_opt:.4f} m")
88      print(f"Optimal Inlet Pressure (P0): {P0_opt / 1e5:.2f} bar")
89      print(f"Optimal Bed Porosity (por): {por_opt:.4f}")
90      print(f"Optimal Number of Tubes (N): {int(N_opt)}")
91      print(f"Optimal Catalyst Diameter (dp): {dp_opt * 1000:.2f} mm")
92      print(f"Optimal Reactor Length (L): {L_opt:.2f} m")
93      print(f"KW at Optimum: {KW_opt:.4f}")
94  else:
95      print("Optimisation failed:", result.message)
```