Reverse Water–Gas Shift PINN

rWGS z-PINN / Digital Twin:
First-Principles Model and Variables

Scope and Motivation

This document describes a physics-informed neural network (PINN) prototype for a one-dimensional axial fixed-bed reactor performing the reverse water–gas shift (rWGS) reaction. The model is intended as a foundation for:

- Prediction of axial temperature profiles $T(z)$ (and optionally species profiles $F_i(z)$),
- Inference of catalyst deactivation a (coking or poisoning) from outlet conversion X_{CO_2} and selectivity S_{CO} only,
- Transfer learning from legacy steady-state datasets,
- Identification of kinetic parameters (k_0, E) via Monte-Carlo or Bayesian sampling under PINN residual constraints.

Each experimental run is treated as a steady operating point. Time dependence is represented implicitly through space time or residence time changes induced by variations in GHSV or flow.

1 Reactor and Operating Space

1.1 Geometry

The reactor is modeled as a one-dimensional plug-flow reactor along the axial coordinate z:

$$L = 0.20\,\mathrm{m} \tag{1}$$

Example axial sensor locations:

$$z \in \{0,\ 0.05,\ 0.10,\ 0.15,\ 0.20\}\ \mathrm{m} \tag{2}$$

1.2 Typical Operating Conditions

$$T_{\mathrm{in}} \in [823, 1223]\ \mathrm{K} \quad (550\text{–}950\,^{\circ}\mathrm{C}) \tag{3}$$

$$p \in [1, 10]\ \mathrm{bar(a)} \quad (\text{default } 5\ \mathrm{bar}) \tag{4}$$

$$\mathrm{H_2/CO_2} = 3 \tag{5}$$

Corresponding inlet mole fractions:

$$y_{\mathrm{CO_2,in}} = 0.25, \qquad y_{\mathrm{H_2,in}} = 0.75 \tag{6}$$

1.3 Catalyst Loading

A lumped catalyst loading per axial length is assumed:

$$W' = 0.10\,\mathrm{kg_{cat}\,m^{-1}} \tag{7}$$

$$W = W'L = 0.02\,\mathrm{kg_{cat}} \tag{8}$$

2 Reaction System

2.1 Main Reaction

$$\mathrm{CO_2 + H_2 \rightleftharpoons CO + H_2O} \tag{9}$$

Stoichiometric coefficients:

$$\nu_{\mathrm{CO_2}} = -1, \qquad \nu_{\mathrm{H_2}} = -1, \qquad \nu_{\mathrm{CO}} = +1, \qquad \nu_{\mathrm{H_2O}} = +1 \tag{10}$$

2.2 Thermochemistry

The rWGS reaction is endothermic:

$$\Delta H_{\mathrm{rWGS}} = +41{,}000\ \mathrm{J\,mol^{-1}} \tag{11}$$

3 State Variables and Definitions

3.1 State Vector

The minimal state vector along the reactor axis is

$$\mathbf{x}(z) = [T(z), F_{\mathrm{CO_2}}(z), F_{\mathrm{H_2}}(z), F_{\mathrm{CO}}(z), F_{\mathrm{H_2O}}(z)] \tag{12}$$

3.2 Derived Quantities

Total molar flow:

$$F_T(z) = \sum_i F_i(z) \tag{13}$$

Mole fractions:

$$y_i(z) = \frac{F_i(z)}{F_T(z)} \tag{14}$$

Partial pressures:

$$p_i(z) = y_i(z)\,p \tag{15}$$

with p in Pa (1 bar $= 10^5$ Pa).

3.3 Performance Indicators

$\mathrm{CO_2}$ conversion:

$$X_{\mathrm{CO_2}} = \frac{F_{\mathrm{CO_2,in}} - F_{\mathrm{CO_2,out}}}{F_{\mathrm{CO_2,in}}} \tag{16}$$

CO selectivity (carbon basis):

$$S_{\mathrm{CO}} = \frac{F_{\mathrm{CO,out}} - F_{\mathrm{CO,in}}}{(F_{\mathrm{CO,out}} - F_{\mathrm{CO,in}}) + (F_{\mathrm{CH_4,out}} - F_{\mathrm{CH_4,in}})} \tag{17}$$

If methane is negligible:

$$S_{\mathrm{CO}} \approx \frac{F_{\mathrm{CO,out}} - F_{\mathrm{CO,in}}}{F_{\mathrm{CO_2,in}} - F_{\mathrm{CO_2,out}}} \tag{18}$$

4 First-Principles Plug-Flow Model

4.1 Mass Balances

For a reaction rate $r(z)$ per catalyst mass:

$$\frac{dF_i}{dz} = \nu_i \, r(z) \, W' \tag{19}$$

Explicitly:

$$\frac{dF_{\mathrm{CO_2}}}{dz} = -rW' \tag{20}$$

$$\frac{dF_{\mathrm{H_2}}}{dz} = -rW' \tag{21}$$

$$\frac{dF_{\mathrm{CO}}}{dz} = +rW' \tag{22}$$

$$\frac{dF_{\mathrm{H_2O}}}{dz} = +rW' \tag{23}$$

4.2 Energy Balance

$$\frac{dT}{dz} = \frac{-\Delta H_{\mathrm{rWGS}} \, rW' + UA'(T_w - T)}{F_T C_{p,\mathrm{mix}}} \tag{24}$$

Typical toy values:

$$C_{p,\mathrm{mix}} = 35 \, \mathrm{J\,mol^{-1}\,K^{-1}} \tag{25}$$

$$UA' = 15 \, \mathrm{W\,K^{-1}\,m^{-1}} \tag{26}$$

5 Kinetics

5.1 Arrhenius Law

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right), \qquad R = 8.314 \, \mathrm{J\,mol^{-1}\,K^{-1}} \tag{27}$$

5.2 Equilibrium Approximation

$$\ln K_{\mathrm{eq}}(T) = A + \frac{B}{T} \tag{28}$$

Typical toy constants:

$$A = -3.0, \qquad B = 4000 \, \mathrm{K} \tag{29}$$

5.3 Reaction Rate Expression

$$r = a \, k(T) \left(p_{\mathrm{CO_2}} p_{\mathrm{H_2}} - \frac{p_{\mathrm{CO}} p_{\mathrm{H_2O}}}{K_{\mathrm{eq}}(T)} \right) \tag{30}$$

Here $a \in (0, 1]$ denotes catalyst activity.

6 Deactivation Model

For synthetic studies, activity may be prescribed per run index n:

$$a(n) = \exp\left(-\frac{n}{\tau}\right), \qquad \tau \approx 60 \tag{31}$$

In real applications, a is inferred implicitly from deviations in $X_{\mathrm{CO_2}}$, S_{CO}, and reconstructed temperature profiles.

7 PINN Formulation

7.1 Neural Approximation

The neural network approximates:

$$\hat{\mathbf{x}}(z;\theta) = \left[\hat{T}, \hat{F}_{\mathrm{CO_2}}, \hat{F}_{\mathrm{H_2}}, \hat{F}_{\mathrm{CO}}, \hat{F}_{\mathrm{H_2O}}\right] \tag{32}$$

7.2 Physics Residuals

Mass balance residuals:

$$\mathcal{R}_{F_i}(z) = \frac{d\hat{F}_i}{dz} - \nu_i \, \hat{r} W' \tag{33}$$

Energy residual:

$$\mathcal{R}_T(z) = \frac{d\hat{T}}{dz} - \frac{-\Delta H \, \hat{r} W' + U A'(T_w - \hat{T})}{\hat{F}_T C_{p,\mathrm{mix}}} \tag{34}$$

7.3 Loss Function

$$\mathcal{L}_{\mathrm{data}} = \sum_k \left| \hat{T}(z_k) - T_{\mathrm{meas}}(z_k) \right|^2 \tag{35}$$

$$\mathcal{L}_{\mathrm{phys}} = \sum_{z_c} \left(|\mathcal{R}_T(z_c)|^2 + \sum_i |\mathcal{R}_{F_i}(z_c)|^2 \right) \tag{36}$$

$$\mathcal{L}_{\mathrm{bc}} = |\hat{T}(0) - T_{\mathrm{in}}|^2 + \sum_i |\hat{F}_i(0) - F_{i,\mathrm{in}}|^2 \tag{37}$$

Total loss:

$$\mathcal{L} = \lambda_{\mathrm{data}} \mathcal{L}_{\mathrm{data}} + \lambda_{\mathrm{phys}} \mathcal{L}_{\mathrm{phys}} + \lambda_{\mathrm{bc}} \mathcal{L}_{\mathrm{bc}} \tag{38}$$

8 Parameter Identification

Kinetic parameters are treated as global unknowns:

$$E \sim \mathcal{U}(70, 140) \ \mathrm{kJ\,mol^{-1}} \tag{39}$$

$$\log_{10} k_0 \sim \mathcal{U}(-8, -2) \tag{40}$$

Candidate sets are evaluated by minimizing outlet mismatches and physics residual norms, optionally using transfer learning to accelerate convergence.