

Mechanistic Two-Phase Fluidized-Bed Reactor Model for Catalytic Methane Pyrolysis

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Abstract

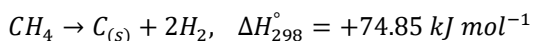
A model of a bubbling fluidized-bed reactor for catalytic methane pyrolysis over a $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst is created, checked, and validated using three published experimental datasets. The model is one-dimensional and has two phases, and it follows the Kunii-Levenspiel principle. An axial energy balance, hydrogen inhibition, interphase mass transfer, gas-solid hydrodynamics, and power-law kinetics are all part of the model. The numerical verification reveals that a fourth-order Runge-Kutta solution with 200 axial nodes that is fixed-step agrees with an adaptive Dormer-Prince RK45 solution in terms of methane conversion to within 3×10^{-7} , conserves energy and hydrogen to a better than 0.1% degree, and approaches thermodynamic equilibrium but never surpasses it. The model forecasts a methane conversion of 65.2% and a hydrogen mole fraction of 68.5% at the base case conditions of 900 °C, 1 bar, $U_0/U_{mf} = 3$, 2 kg catalyst, and 80% CH_4 . The model predicts velocity and catalyst-loading effects that are conservative for design, but surpass the 15% acceptance requirement. It also accurately reproduces calibrated temperature effects within 5% and the direction of all trends versus three literature fluidized-bed datasets. Methane pyrolysis reactors can be physically optimised, surrogate models can be used, and uncertainty can be quantified with this approach

Keywords: Methane Pyrolysis; Fluidized Bed; Kunii-Levenspiel; Catalyst Deactivation; Hydrogen; Reactor Modelling.

I. INTRODUCTION

The shift to an energy system with lower carbon emissions is commonly believed to revolve around hydrogen. Nearly all of the world's 95 million metric tonnes of hydrogen in 2022 came from unregulated fossil fuels, with less than one percent coming from low-emission sources (IEA, 2023). According to the IEA (2019) and Parkinson et al. (2019), the most common method of production, steam methane reforming (SMR), results in the release of about 9 to 10 kg of carbon monoxide for every kilogram of hydrocarbons (HTM) that are generated. We need to find affordable ways to produce hydrogen that doesn't release these pollutants if it's going to play a significant role in decarbonisation.

One such method is methane pyrolysis, which goes by a few other names: methane cracking and thermocatalytic decomposition (TCD). Hydrogen and solid carbon are directly produced from methane:



No CO_2 is produced throughout the reaction as carbon exits as a solid rather than gaseous CO_2 . Endothermic heat requirement of 37.4 kJ per mole of H_2 is lower than steam reforming, and no water-gas shift reactors or CO_2 separation are needed (Muradov & Veziroglu, 2005; Abbas & Wan Daud, 2010; Sanchez-Bastardo et al., 2021). Solid carbon co-products such carbon black, graphite, carbon fibres, and carbon nanotubes can generate additional revenue to offset hydrogen production costs (Dagle et al., 2017; Keipi et al., 2018).

Uncatalyzed thermal pyrolysis needs temperatures over ~1,200 °C due to the C–H bond strength. Nickel, iron, cobalt, and carbonaceous catalysts lower the needed temperature significantly. Carbon from the reaction settles on the catalyst and wraps the active metal, deactivating it continually. Deactivating catalysts is an intrinsic part of the chemistry, affecting catalyst lifetime, regeneration frequency, and process economics (Ashik et al., 2015; Zhou et al., 2017).

The need to handle a rising solid carbon store substantially influences reactor choice. As carbon builds, fixed-bed reactors clog. Fluidized-bed reactors (FBRs) are mature at industrial scale, allow continuous catalyst addition and carbon-laden particle removal, and have outstanding temperature uniformity and heat-transfer rates. Thus, the bubbling fluidised bed is a viable catalytic methane

pyrolysis structure. Its behaviour is complicated: gas passes through a dense emulsion phase in contact with catalyst and bubbles that bypass most particles, and conversion depends on interphase gas exchange. This conduct requires mechanistic two-phase models like the Kunii–Levenspiel model (Kunii & Levenspiel, 1991).

The design of a methane pyrolysis FBR must balance high methane conversion, high hydrogen content in the output gas, and cheap hydrogen cost. Heating increases reaction rate and equilibrium conversion but deactivates catalysts and raises material costs. Increased catalyst supplies boost conversion but increase reactor size and expense. Higher pressures lower equilibrium conversion but reactor volume and compression costs. These problems require multi-objective treatment (Deb, 2001; Deb et al., 2002), but first a reliable mechanistic reactor model is needed.

Development, verification, and validation of a mechanistic MATLAB model of a bubbling fluidized-bed reactor for methane pyrolysis using one-dimensional two-phase hydrodynamics, reaction kinetics with catalyst deactivation, and heat and mass transfer is the goal of this project. Jung et al. (2007), Jang et al. (2009), and Hauser (2022) validate the model against numerical benchmarks, conservation laws, and thermodynamic equilibrium and three published fluidized-bed methane decomposition datasets. Nigeria, which has the highest confirmed natural gas reserves in Africa (>200 TCF) and has proclaimed 2021–2030 a "Decade of Gas," is one of the world's largest associated gas flarers (World Bank, 2023). Methane pyrolysis might produce solid carbon for the tyre, battery, construction and materials sectors while converting some of this gas into low-carbon hydrogen.

II. MATERIALS AND METHODS

2.1 System Definition and Assumptions

The reactor is a continuous bubbling fluidized bed of 0.10 m internal diameter operated at steady state. It contains an iron-based (Fe/Al₂O₃) catalyst of Geldart group B ($d_p = 200 \mu\text{m}$, $\rho_p = 2,500 \text{ kg/m}^3$). The bed is heated through the wall, which is held 25 K above the set-point temperature. Methane, diluted with nitrogen when $y_{\text{CH}_4} < 1$, enters at the set-point temperature through a distributor that generates initial bubbles of 10 mm diameter. Catalyst is added and withdrawn continuously, with a mean cycle time of $t_c = 24 \text{ h}$ before withdrawal with its carbon deposit. The assumptions are:

1. One-dimensional, steady-state flow in the axial direction z ; radial gradients are neglected.
2. Kunii–Levenspiel two-phase behaviour: gas in excess of minimum fluidization flows as bubbles. The emulsion phase is at minimum fluidization conditions, with voidage $\epsilon_{mf} = 0.45$. A small fraction of solids ($\gamma_b = 0.005 \text{ m}^3 \text{ solids per m}^3 \text{ bubble}$) is dispersed in the bubbles.
3. Both phases are in plug flow and exchange gas through the interphase coefficient K_{be} . Gas and solids are at the same local temperature, and the gas obeys the ideal gas law.
4. Particles are isothermal, with no elutriation and no agglomeration in the base model. Carbon remains on the catalyst and is withdrawn with it.
5. Pressure drop across the bed is small compared with the operating pressure, so the pressure is uniform.
6. Catalyst activity decays by first-order deactivation, and the bed contains a residence-time-averaged activity $\bar{a}$

2.2 Decision Variables

Five decision variables define a reactor design: reactor temperature (800–1,100 °C), operating pressure (1–5 bar), fluidization ratio U_0/U_{mf} (2–5), catalyst mass (0.5–5 kg), and methane mole fraction in the feed (0.5–1.0). The base case is 900°C, 1 bar, $U_0/U_{mf} = 3$, 2 kg catalyst, $y_{\text{CH}_4} = 0.8$. The temperature bound of 1,100°C enforces the material limit if the reactor wall and internals. Fixed parameters: reactor internal diameter 0.10m; particle diameter 200 μm ; particle density 2,500 kg/m^3 ; $\epsilon_{mf} = 0.45$; initial bubble diameter 0.010m; solids in bubbles 0.005; wall temperature above set-point 25K; catalyst cycle time 24h; reaction order in CH₄ $n = 1.0$; activation energy of deactivation $E_d = 100 \text{ kJ/mol}$; reference temperature for k_d 1,173.15K; ambient temperature 298.15K.

2.3 Mathematical Model

a) Hydrodynamics (Kunii–Levenspiel two-phase model): Gas density and viscosity are evaluated at the set-point temperature and feed composition. The minimum fluidization velocity is given by the Wen and Yu (1966) correlation,

$$Re_{mf} = (33.7^2 + 0.0408 Ar)^{0.5} - 33.7, \quad U_{mf} = \frac{Re_{mf} \mu_g}{d_p \rho_g} \quad (2)$$

and the superficial velocity is $U_0 = (U_0/U_{mf}) \cdot U_{mf}$. The bubble diameter grows linearly with height above the distributor, limited to 90 % of the reactor diameter:

$$D_b(z) = \min \left[D_{b0} + 0.27 (U_0 - U_{mf})^{0.5} z, 0.9 D \right] \quad (3)$$

The bubble rise velocity, bubble volume fraction and interphase exchange coefficient (Sit & Grace, 1981) are

$$U_b = U_0 - U_{mf} + 0.711 \sqrt{g D_b}, \quad \delta = \frac{U_0 - U_{mf}}{U_b} \quad (4)$$

$$K_{be} = \phi_{be} \frac{6}{D_b} \left[\frac{U_{mf}}{3} + \left(\frac{4 D_{AB} \varepsilon_{mf} U_b}{\pi D_b} \right)^{0.5} \right] \quad (5)$$

where D_{AB} is the $\text{CH}_4\text{--H}_2$ diffusivity, taken as $7.3 \times 10^{-5} (T/298)^{1.75/P}$ m²/s, and ϕ_{be} is a correction factor (nominally 1). The bed height at minimum fluidization is $H_{mf} = W_{cat}/[\rho_p(1 - \varepsilon_{mf})A]$, and the expanded bed height is $H_f = H_{mf}/(1 - \delta_{mid})$.

b) Kinetics with catalyst deactivation: The rate per kg catalyst is:

$$r = k_0 \bar{a} \exp \left(-\frac{E_a}{RT} \right) p_{\text{CH}_4}^n \left(1 - \frac{p_{\text{H}_2}^2}{K_p p_{\text{CH}_4}} \right) \frac{1}{1 + K_H p_{\text{H}_2}} \eta_{\text{contact}} \quad (6)$$

Where:

K_H is a hydrogen adsorption inhibition constant (fitted), and η_{contact} is a contact efficiency for Geldart C beds;

$$\eta_{\text{contact}} = 1 - \exp \left[-\alpha \left(\frac{U_0}{U_{mf}} - 1 \right) \right] \quad (7)$$

With α fitted to the carbon-black datasets. Deactivation remains first order:

$$\frac{da}{dt} = -k_d(T)a, \quad a(0) = 1, \quad k_d(T) = k_{d,ref} \exp \left[-\frac{E_d}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (8)$$

Mean bed activity:

$$\bar{a} = \frac{1 - e^{-k_d t_c}}{k_d t_c} \quad (9)$$

c) Mass and energy balances: Molar balances are written for CH_4 , H_2 and N_2 (index i) in the bubble (b) and emulsion (e) phases. With A the reactor cross-section and v_i the stoichiometric coefficients (-1 for CH_4 , $+2$ for H_2 , 0 for N_2):

$$\frac{dF_{i,b}}{dz} = -K_{be} \delta A C_T (y_{i,b} - y_{i,e}) + v_i r_b \rho_p \gamma_b \delta A \quad (10)$$

$$\frac{dF_{i,e}}{dz} = +K_{be} \delta A C_T (y_{i,b} - y_{i,e}) + v_i r_e \rho_p (1 - \varepsilon_{mf})(1 - \delta) A \quad (11)$$

where $CT = P/RT$ is the total molar concentration and y the mole fractions. Inlet flows are split between phases according to two-phase theory, with a fraction U_{mf}/U_0 entering the emulsion. The energy balance on the flowing gas is

$$\sum_i F_i C_{p,i} \frac{dT}{dz} = h_w \pi D (T_w - T) - \Delta H_r(T) (R_b + R_e) - U_w \pi D (T - T_{amb}) \quad (3.11)$$

where R_b and R_e are the reaction rates per unit height, h_w is the bed-to-wall heat transfer coefficient, U_w the heat-loss coefficient, and $\Delta H_r(T) = 89,850 + 7.9(T - 1,000)$ J/mol from JANAF data. Heat capacities are polynomial fits to NIST data. Cumulative wall heat input and heat loss are integrated alongside the balances.

d) Model outputs: The model returns methane conversion $X_{\text{CH}_4} = 1 - F_{\text{CH}_4,\text{out}}/F_{\text{CH}_4,\text{in}}$, the hydrogen mole fraction of the reactor effluent Y_{H_2} , the carbon production rate, outlet temperature, heat duties and hydrodynamic properties. A design is described by $y = \text{FBR}_{\text{model}}(T, P, U_0/U_{mf}, W_{\text{cat}}, y_{\text{CH}_4}; \theta)$.

2.4 Numerical Solution and Verification

Eight coupled ordinary differential equations (six species balances and the energy balance, plus the heat-duty integrals) are integrated over the normalised height $\zeta = z/H_f$ from 0 to 1. The MATLAB implementation uses ode45 with a relative tolerance of 10^{-6} . For large Monte Carlo campaigns, the identical equations were implemented in vectorised form in Python and integrated with the classical fourth-order Runge–Kutta method on a uniform grid. The MATLAB code was executed in GNU Octave (which provides the same ode45 algorithm) and reproduced the Python conversions to six significant figures at the base case ($X = 0.651850$)

and at two other designs. Samples whose fixed-step solution was non-physical were automatically re-integrated on a four-times finer grid.

The verification procedure comprised:

- (1) Solver verification: comparison of the fixed-step solution with the adaptive Dormand–Prince RK45 solution at $\text{rtol } 10^{-6}$ for six designs spanning the design space;
- (2) Grid independence: solution with 50, 100, 200 and 400 axial integration nodes, compared with a 3,200-node reference, at the base case and two extreme corners;
- (3) Conservation checks: closure of the hydrogen element balance and of the overall energy balance;
- (4) Thermodynamic consistency: with a very active catalyst ($k_0 = 105$, $\phi_{be} = 20$), the model must approach, but never exceed, the equilibrium conversion at the outlet temperature, at all temperatures and pressures.

2.5 Experimental Validation Data

Three published fluidized-bed methane decomposition studies with complete operating information were used. In all three, pure methane (or 98% natural gas) was fed at atmospheric pressure to an electrically heated bubbling bed of about 0.055m diameter, and the bed temperature was measured and controlled. The beds were modelled as isothermal at the measured temperature, using the same hydrodynamic, interphase-transfer and rate equations as the design model, changing only geometry, particle properties, bed mass and gas flow.

Dataset A (Jang et al., 2009): quartz FBR, 0.055 m I.D., 1.0m high; carbon black (HI20/HI170), 50-200g; 850-900°C; atm; pure CH₄; 1-3 Umf. Eight quasi-steady conversions.

Dataset B (Jung et al., 2007): same reactor; carbon black N330 (dp, eff = 153µm), 100g; 850-925 °C; 1-3Umf. Five quasi-steady conversions.

Dataset C (Hauser, 2022): electrically heated FBR, 54.4mm I.D.; Fe powder diluted with olivine (63-72wt% Fe), 0.8-1.1kg; dsv = 196µm; 650-950°C; 71mm/s CH₄ (ambient basis); atm. Four H₂ production rates converted to conversion.

Quasi-steady conversions for Datasets A and B were digitized from the published figures as the average of points between 4 and 8h on stream (Dataset B temperature series: 2.3-4h), when carbon-black activity had stabilized. The reading uncertainty is about ±0.5 percentage points. For Dataset C, methane conversion was calculated from the reported hydrogen production rate as $X = \frac{[m'_H]_2}{2(F_{CH_4} M_{(H_2)})}$, with $[F_{CH_4}]_4 = 24.3$ mol/h from a superficial velocity of 71mm/s at 25°C and 1 atm in the 54.4mm tube. The particle diameter of the Fe-olivine mixture was set so that the Ween-Yu correlation reproduces its measured Umf of 98.8mm/s (air, 20°C).

The procedure separates calibration from prediction:

Carbon-black datasets (A and B): the effective rate constant k_0 , activation energy E_a , hydrogen inhibition constant K_H and contact-efficiency parameter α are fitted by least squares to the temperature series at 1Umf and 100g. the effects of gas velocity (2 and 3 Umf) and catalyst loading (50, 150, 200g) are then predicted without further fitting.

Iron dataset (C): the Fe-catalyst kinetics E_a and k_0 are fitted to two points (IO1 650°C and IO1 900°C). The remaining two point (IO1 950°C and IO2 ~900°C) are used as independent validation.

The acceptance criterion is a relative error below 15%

III. RESULTS AND DISCUSSION

3.1 Base-Case Hydrodynamics

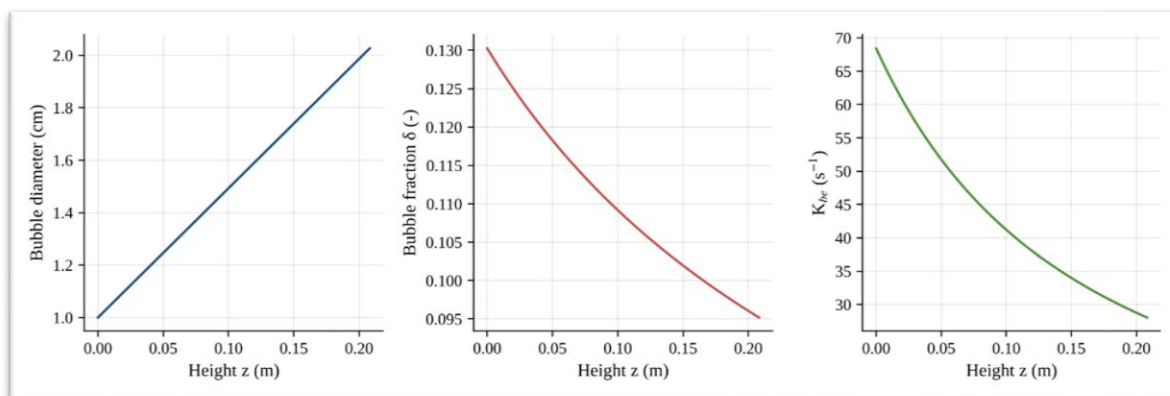


Figure 4.1 Axial Profiles of Bubble Diameter, Bubble Fraction and Interchange Coefficient at the Base Case

At the base case (900°C, 1 bar, $U_0/U_{mf} = 3$, $W_{cat} = 2\text{ kg}$, $y_{CH_4} = 0.8$), the gas density is 0.190 kg/m^3 , gas viscosity $3.56 \times 10^{-5}\text{ Pa}\cdot\text{s}$, Archimedes number 29.3, $Re_{mf} = 0.0177$, minimum fluidization velocity 0.0167 m/s , and superficial velocity 0.0500 m/s . The bed height at minimum fluidization is 0.185 m and the expanded bed height 0.208 m . The bubble diameter grows from 1.0 cm at the distributor to 2.0 cm at the bed surface. The bubble fraction decreases from 0.130 at the distributor to 0.095 at the bed surface, and the interchange coefficient decreases from 68 to 28 s^{-1} .

Geldart B particles bubble in the reactor. The bubble diameter develops from 1.0 cm at the distributor to 2.0 cm at the bed surface, following the Davidson-Harrison correlation for bubble growth by coalescence. As bubbles accelerate, the bubble fraction decreases from 0.130 to 0.095 and the interchange coefficient decreases from 68 to 28 s^{-1} due to the Sit-Grace correlation diffusive term varying as $D_b^{-1.5}$ (Sit & Grace, 1981). As height increases, the bed transfers methane from bubbles to the catalyst-rich emulsion less efficiently. Practically, the higher section of the bed contributes less to conversion than the lower section, and taller beds would have declining results unless internals or distributor design restrict bubble size. This bubbling behaviour of Geldart B solids is well documented (Kunii and Levenspiel, 1991). The minimal fluidisation velocity of 0.0167 m/s from the Wen-Yu correlation (Wen & Yu, 1966) matches Geldart B particles of similar size and density. The fluidisation ratio of 3 at 0.0500 m/s is common for bubbling fluidised beds. The settled bed height of 0.185 m and enlarged bed height of 0.208 m are suitable for a 0.10 m reactor with 2 kg catalyst.

3.2 Base-Case Conversion, Composition and Temperature Profiles

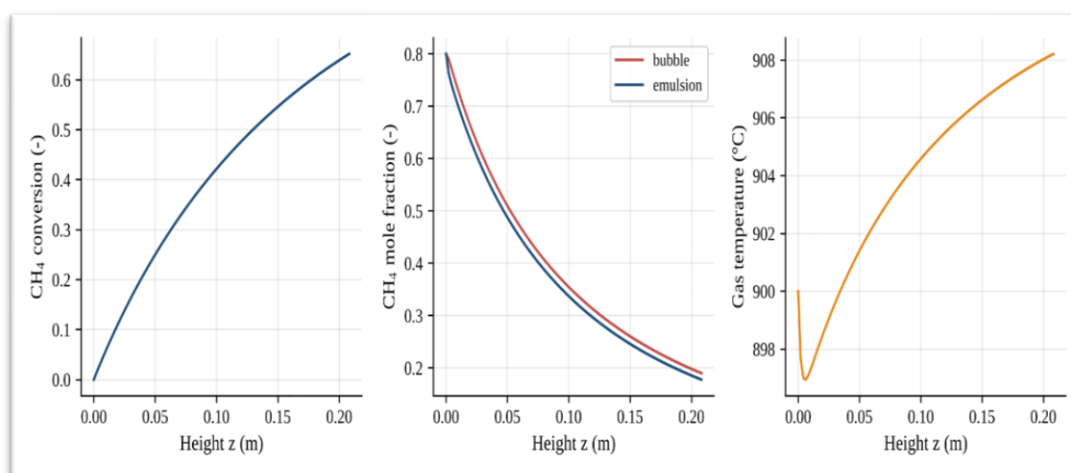


Figure 4.2 Axial Profiles of Methane Conversion, Phase Compositions and Gas Temperature at the Base Case

The hydrogen mole fraction of the effluent is 0.685 in the base case, while methane conversion is 0.652 . Activity for the mean catalyst is 0.794 . At 900°C , the equilibrium conversion X_{eq} is 0.9662 , and the equilibrium constant K_p is 49.80 bar . Its temperature at discharge is 908.2°C . The reaction enthalpy is 192 W , the heat loss is 287.4 W , the wall heat input is 481.2 W , and the sensible heating of the gas is 2 W . At the exit, the mole percentage of CH_4 in the bubble phase is 0.190 , while in the emulsion phase it is 0.178 . Near the distributor, the gas temperature drops by around 3 K , but it climbs to 908.2°C at the output.

The reactor is kinetically regulated since the base-case conversion of 0.652 is substantially below the equilibrium conversion of 0.966 at 900°C . Ammendola et al. (2008) observed that reaction kinetics rather than equilibrium limit methane pyrolysis in fluidized

beds, especially at moderate temperatures. The mean catalyst activity of 0.794 shows strong deactivation even at the base case, similar to Ashik et al. (2015) and Zhou et al. (2017) for iron-based catalysts. Because bubble and emulsion methane mole fractions are close (0.190 and 0.178 at the outflow), interphase mass transfer is faster than reaction for these small bubbles. This design discovery is crucial: the two-phase model acts as a single-phase plug-flow reactor for small bubbles. The Kunii–Levenspiel model forecasts that larger bubbles at increased gas velocities will exacerbate bypass and conversion (Kunii & Levenspiel, 1991). The kinetically controlled domain is shown by the hydrogen mole fraction of 0.685, below equilibrium at 0.966. The endothermic process first cools the gas, but wall heating gradually dominates. Following a 3-K decrease, the distributor temperature increases to 908.2 °C. Out of the 481 W of heat that was delivered, the tiny 0.10 m reactor loses 287 W. Reduced heat loss at the plant scale is achieved by maintaining a low surface-to-volume ratio.

3.3 Verification of the Numerical Solution

The fixed-step RK4 solution with 200 axial nodes agreed with the adaptive RK45 solution to within 3×10^{-7} in conversion. At the base case, 100 nodes were sufficient. At corner configurations with biggest catalyst inventories and lowest gas flows, 50 or 100 nodes were unstable. With 200 nodes the solution was steady and grid-independent everywhere. The MATLAB/Octave ode45 solution and the Python solution both provided $X = 0.651850$ in the base case, agreeing to six significant digits. The hydrogen element balance closed to a relative inaccuracy of 4×10^{-16} , and the energy balance closed to 0.07% (193.77 W supplied vs 193.64 W consumed). The model converged to the equilibrium conversion at the outlet temperature to four decimal places at all 14 situations examined.

The agreement between RK4 and RK45 in conversion within 3×10^{-7} demonstrates the fixed-step solver is suitable for this problem. The stiff relationship between energy balancing and wall heat transfer causes corner designs (high catalyst inventory, low gas flow) to be unstable at 50 or 100 nodes. Practically, the model cannot be run with a coarse grid across the design space; robust optimisation requires 200 nodes. This follows Shampine and Reichelt (1997)'s stringent ODE system recommendations. A hydrogen element balance closure of 4×10^{-16} and an energy balance closure of 0.07% reveal that the model accurately conserves mass and energy. In surrogate-based optimisation, Forrester et al. (2008) underlined the need for these tests for reactor models used for design.

3.4 Thermodynamic Consistency

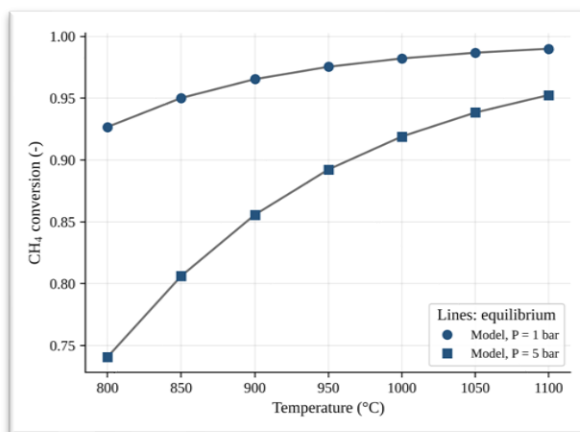


Figure 4.3 Model Conversion with a Highly Active Catalyst Compared with Thermodynamic Equilibrium

Using a very active catalyst ($k_0 = 10^5$, $\phi_{be} = 20$, $W_{cat} = 2$ kg), the model reached equilibrium conversion at outlet temperature to four decimal places in all 14 situations. Model approached equilibrium but never exceeded it. Temperature increases equilibrium conversions and pressure decreases them (Abbas & Wan Daud, 2010). The kinetic model never exceeds equilibrium, proving its thermodynamic consistency. The model accurately predicts thermodynamic restrictions spanning the design region from 800 to 1,100 °C and 1 to 5 bar.

3.5 Parametric Study

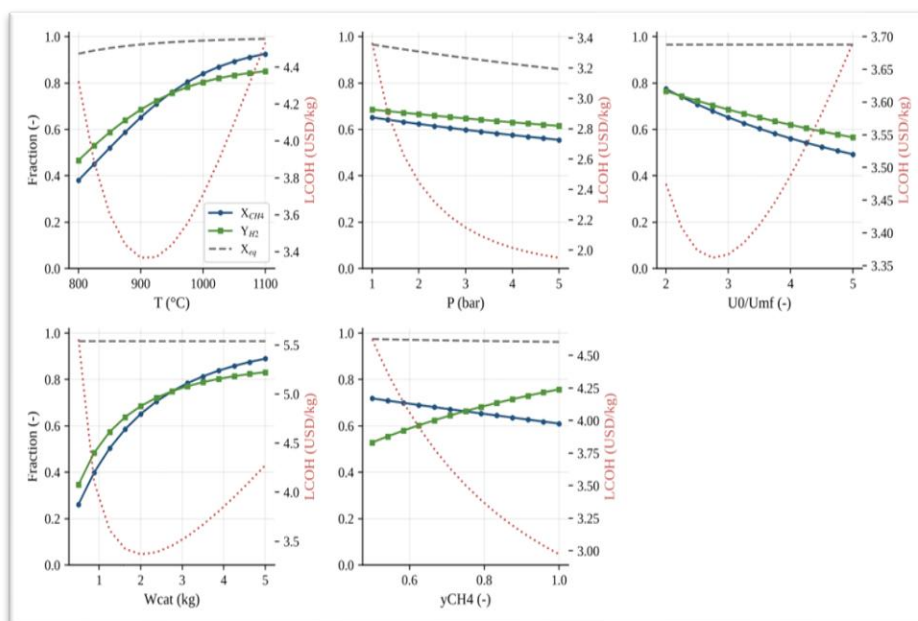


Figure 4.4 Effect of the Decision Variables on Conversion, H₂ Mole Fraction and LCOH (Other Variables at Base Case, Nominal Parameters)

Conversion increases most with temperature, from 0.380 at 800 °C to 0.926 at 1,100 °C. Low LCOH ranges from 3.37 USD/kg near 900–925 °C to 4.53 USD/kg at 1,100 °C. Faster deactivation (k_d increases 4.4-fold from 900 to 1,100 °C), higher material factors, and higher heat demand counterbalance conversion gain above this temperature. High conversion temperatures reduce catalyst lifespan and increase cost, a key design trade-off. Thus, the optimal LCOH temperature is substantially lower than the maximum conversion temperature. Keipi et al. (2016) and Lumbers et al. (2022) found that methane pyrolysis' economic optimum is below maximal conversion temperature.

Rising pressure from 1 to 5 bar lowers conversion from 0.652 to 0.555 and LCOH from 3.37 to 1.95 USD/kg because each reactor processes five times more gas and needs less compression before the PSA. Low pressure is thermodynamically optimal, yet high pressure is economic. Pressure reduces design costs but reduces conversion.

Shorter contact time and more bubble bypassing reduce conversion from 0.774 to 0.493 when fluidisation ratio is increased from 2 to 5. LCOH is lowest at $U_0/U_{mf} \approx 2.7$. Increased catalyst mass increases conversion from 0.262 to 0.890 with declining returns. Increasing methane feed percentage from 0.5 to 1.0 leads to poorer conversion (0.718 to 0.610) but higher effluent H₂ fraction (0.529 to 0.758) and lower LCOH (4.62 to 2.97 USD/kg) due to reduced diluent heating, compression, and separation. These findings mirror thermocatalytic methane decomposition literature (Abbas & Wan Daud, 2010; Ashik et al., 2015; Keipi, 2016).

3.6 Experimental Validation against Published Fluidized Data

The model kept calibrated temperature effects within 5% but underestimated catalyst loadings by 21–24% and conversion at higher gas velocities by 27–49%. The model only matched iron-catalyzed conversions within 1.5 using unfitted kinetics. These mistakes are produced by poor gas–solid contact in cohesive Geldart C carbon-black beds, hydrogen suppression of carbon catalyst rates, and iron activity's dependence on activation history and carbon deposition. The model recreated both carbon-black datasets' temperature series within 5% (six points; mean absolute error 2.1%) with two estimated kinetic parameters. The fitted activation energy for Dataset A, 184 kJ/mol, matches Jang et al. (2009)'s 200. Dataset B had a lower apparent result (71 kJ/mol) due to the shorter N330 carbon black conversion range between 850 and 925 °C. According to Borghei et al. (2010) and Zavarukhin and Kuvshinov (2004), carbon catalyst apparent activation energies vary with catalytic preparation and operating circumstances.

The gas velocity underprediction confirms Jung et al. (2007) and Jang et al. (2009), which attributed incomplete fluidisation to poor gas–solid contact at 1 U_{mf} in cohesive Geldart C carbon-black beds. As forceful bubbling mixes the bed at higher velocities, contact efficiency increases and conversion declines less than expected by a plug-flow model. It would perform similarly as hydrogen inhibition suppresses carbon catalyst rate most at low flow and high conversion. Neither impact is in the current model, explaining the systematic underprediction at higher velocities. The model predicted a nearly proportional conversion rise with bed mass at 1 U_{mf} , however the facts were not. Again, Jang et al. (2009) blamed non-uniform gas distribution in taller Geldart C carbon black beds.

Without fitting, nominal Fe kinetics predicted 22–40% conversion at 900–950 °C, compared to 19–56% in Hauser's Fe–olivine bed (2022). The prediction at 650 °C was inaccurate (-76%), with errors from -42% to +42% at 900–950 °C. At identical temperatures, IO1 has 36.8% at 900 °C and IO2 19.4% at 920. Hauser (2022) and Zhou et al. (2017) found that activation history, carbon deposition, and carbon self-catalysis greatly affect iron activity. Model projections match experimental data at 900–950 °C. The low-temperature result shows fresh iron powder has a lower apparent activation energy than 100 kJ/mol.

Although calibrated temperature effects met Level 3 standards (error < 15%), anticipated velocity, loading, and iron-kinetics impacts did not. All trends are predicted by the thermodynamically and numerically sound model. In small beds of cohesive carbon black, it overstates conversion loss at higher gas velocity, and unfitted kinetics only replicate iron-catalyzed conversion within 1.5.

Both implications follow. Using Geldart B particles at $U_0/U_{mf} = 2-3$, robust designs ensure conservative hydrodynamic error, making the bubbling-bed model more acceptable. Biased models underestimate high-velocity conversion. The iron data scatter ($\pm 50\%$) between runs surpasses the $\pm 28\%$ (one standard deviation) provided to k_0 in the uncertainty analysis. Using a narrow k_0 distribution suggests that kinetic parameters are the main uncertainty.

IV. CONCLUSION

A one-dimensional, steady-state, two-phase FBR model for catalytic methane pyrolysis has been developed, verified and validated. The model was solved accurately (fixed-step and adaptive solutions agree to 3×10^{-7} in conversion; 200 axial nodes are grid-independent across the design space, whereas 100 nodes are not in its stiff corners). It conserves mass and energy (closure better than 0.1%) and reaches, but never exceeds, thermodynamic equilibrium. At the base case (900 °C, 1 bar, $U_0/U_{mf} = 3$, 2 kg catalyst, 80% CH₄) it predicts 65.2% methane conversion and 68.5% H₂ in the effluent. Conversion increases with temperature and catalyst mass and decreases with pressure, fluidization ratio and dilution. Against three published fluidized-bed datasets, the model reproduced calibrated temperature effects within 5% and the direction of all trends. Predicted effects of gas velocity (errors 27–49%), catalyst loading (21–24%) and unfitted iron kinetics (within a factor of about 1.5) did not meet the 15% criterion. The velocity bias is conservative, since the model underpredicts conversion at higher velocities.

Recommendations for future work include: re-fitting E_a , k_0 and k_d to time-resolved fluidized-bed measurements on the chosen iron catalyst, and widening the k_0 distribution (the run-to-run scatter of about $\pm 50\%$ in the iron data of Hauser (2022) exceeds the $\pm 28\%$ assumed here) before using absolute performance values for detailed design. The rate expression should be extended with hydrogen inhibition and a contact-efficiency correction for poorly fluidizing (Geldart C) materials, which together explain the weaker-than-predicted velocity and loading effects in the carbon-black datasets. The hydrodynamic scale-up assumptions should be validated with CFD or pilot-scale data, since bubble growth and wall heat transfer differ between a 0.10 m laboratory reactor and an industrial reactor with immersed heating surfaces.

The study provides a reusable MATLAB implementation of the reactor model, which can support teaching and research in process modelling and simulation

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Conflict of Interest

The authors declare no conflict of interest.

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