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Executive Summary of the Thesis

Kinetic modeling of deactivation over methanation catalysts

Laurea Magistrale in Chemical Engineering - Ingegneria Chimica

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1. Introduction

The catalytic methanation of carbon oxides is a cornerstone reaction in Power-to-Gas (PtG) systems, industrial decarbonisation strategies, and the upgrading of biomass-derived syngas to synthetic natural gas (SNG). In PtG applications, surplus renewable electricity—generated during periods of high wind or solar output, produces hydrogen via water electrolysis; this hydrogen is then reacted with CO or CO_2 over a supported nickel catalyst to form methane, which can be injected directly into the existing natural gas grid. The methanation route thus provides a pathway for long-term, large-scale energy storage using existing infrastructure, bridging the temporal mismatch between intermittent renewable generation and dispatchable energy demand. The economic attractiveness of SNG production rests on its compatibility with existing distribution networks and end-use appliances, avoiding the capital expenditure of dedicated hydrogen infrastructure.

In the biomass-to-SNG route, syngas produced by gasification of lignocellulosic feedstock is upgraded to pipeline-quality methane via the same catalytic process, offering a carbon-neutral fuel cycle when the CO_2 released upon combustion equals the biogenic carbon originally captured. Both routes rely on the same reaction chemistry and face identical challenges regarding catalyst stability and reactor thermal management.

The two principal methanation reactions are the CO methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$, $\Delta H^\circ = -206$ kJ/mol) and the CO_2 methanation or Sabatier reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta H^\circ = -165$ kJ/mol). Both are strongly exothermic and thermodynamically favoured at low temperatures and elevated pressures, but kinetic considerations dictate that commercially viable rates require 300–400°C over Ni/Al_2O_3 catalysts. In adiabatic or poorly cooled fixed-bed reactors, the exothermic heat release generates severe localized temperature peaks (hotspots) that can exceed 600°C at the reactor inlet, far above the optimal kinetic window. Industrial reactor designs therefore employ plate-cooled or multi-tube configurations to manage this thermal runaway, but the effectiveness of the cooling directly determines the severity of the hotspot and, consequently, the rate of catalyst degradation.

These hotspots are not merely a thermal management challenge: they are the primary driver of catalyst deactivation via Boudouard coking, the disproportionation of CO into solid carbon

and CO_2 ($2CO \rightarrow C + CO_2$). The deposited carbon progressively blocks active sites on the catalyst surface, leading to an irreversible loss of activity that manifests as a declining outlet conversion over time on stream. Because the Boudouard reaction rate follows Arrhenius kinetics with an apparent activation energy of approximately 48 kJ/mol, the local coking rate at the hotspot is exponentially sensitive to temperature: a 73°C reduction in hotspot temperature can decrease the instantaneous local deactivation rate by a factor of 25–35. This tight coupling between the thermal profile and the deactivation kinetics makes hotspot suppression the most effective lever for extending catalyst lifetime, more so than changes in feed composition or operating pressure.

Pappagallo et al. [4] recently introduced a pseudodynamic modelling framework that predicts the time-dependent conversion loss in fixed-bed methanation reactors subject to Boudouard coking. Their approach decouples the slow deactivation kinetics from the fast reaction and transport phenomena through a computationally efficient sequence of steady states. However, their study was limited to four inlet temperatures (300–360°C) and did not explore the broader parametric space—including pressure, space velocity, feed composition, and heat transfer—that governs reactor design. Furthermore, no comparison was made between conventional packed-bed and structured catalyst configurations (monoliths, foams) that offer enhanced heat transfer and are commercially available.

The present thesis addresses these gaps through two objectives. First, a systematic seven-parameter sensitivity analysis is conducted to establish the summary of operating parameter influence on catalyst lifetime and to identify optimal operating windows. Second, three catalyst packing configurations—conventional cylindrical pellets, monolithic honeycomb, and open-cell foam—are compared under identical conditions to quantify the lifetime extension achievable through enhanced heat transfer. The overarching goal is to provide actionable, quantitative guidelines for the design of long-life CO methanation reactors.

2. Methodology

2.1. Pseudodynamic modelling framework

The model exploits the separation of time scales between the phenomena occurring in the reactor: reaction and transport operate on the order of seconds, while deactivation evolves over hundreds of hours. This allows the reactor to be treated as operating in a succession of steady states at progressively decreasing values of the catalyst activity $a(z,t)$, defined as the ratio of the local reaction rate to the rate on a fresh catalyst under identical conditions. The global model reduces to a single ordinary differential equation in time for each axial position:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -r_d(T,\, p_{\mathrm{CO}},\, a) \tag{1}$$

At each integration step, a steady-state reactor submodel is called to compute the axial composition and temperature profiles for the current activity distribution. The reactor submodel is a one-dimensional, pseudo-homogeneous plug-flow model coupling the component mass balance and energy balance along the axial coordinate z:

$$\frac{dF_i}{dz} = \rho_{pb}(1-\epsilon)A\sum_{j=1}^{N_R} a_j(t)\nu_{ij}r_j^0 \tag{2}$$

$$\frac{dT}{dz} = -\frac{\rho_{pb}(1-\epsilon)A}{\dot{m}\hat{c}_P}\sum_{j=1}^{N_R} a_j(t)\Delta h_j^R r_j - \frac{2W}{\dot{m}\hat{c}_P}U(T-T_e) \tag{3}$$

where F_i is the molar flow rate of species i, T the temperature, U the overall heat transfer coefficient, T_e the coolant temperature, and W the channel width. The geometry corresponds to a plate-cooled fixed-bed pilot reactor ($L = 1$ m, $W = 0.5$ m, channel height = 1.5 cm), operated at 8 bar with a stoichiometric 3:1 H_2/CO feed. The steady-state submodel and its coupling with the deactivation kinetics were validated by Pappagallo et al. [4] against pilot-scale experimental data from Moioli et al. [3] and Zhang et al. [5], respectively. The system is solved in MATLAB using the stiff integrator `ode15s`.

2.2. Kinetic and deactivation submodels

Three reactions are considered. The CO_2 methanation follows a Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate expression derived by Koschany et al. [2] ($T_{\text{ref}} = 555$ K), incorporating competitive adsorption of H_2, CO_2, and OH surface species, with a squared denominator reflecting dual-site kinetics. The CO methanation and water–gas shift (WGS) reactions follow the kinetic framework of Kopyscinski et al. [1] ($T_{\text{ref}} = 598.15$ K), which accounts for CO and OH adsorption on the nickel surface. All kinetic constants follow a modified Arrhenius temperature dependence referenced to the respective T_{ref} values, and the equilibrium constants are computed from thermodynamic correlations that ensure thermodynamic consistency for all three reversible reactions. The inclusion of both CO and CO_2 methanation pathways, linked through the WGS equilibrium, captures the complex interplay between the two methanation routes under varying feed compositions.
The deactivation submodel is a semi-empirical power-law expression adapted from Sun et al. and calibrated against the experimental CO methanation data of Zhang et al. [5] at 320, 340, and 360°C, The global deactivation model is expressed as [4]:

$$\frac{da_j}{dt} = -r_{d,j} \cdot a_j^{\beta} \tag{4}$$

$$r_{d,j} = k_{d,j} \cdot p_{CO}^{\alpha} \cdot f_{H_2O} \tag{5}$$

where $k_{d,j}(T) = k_{d,j}^0 \exp(-E_{d,j}/RT)$ with $E_d =$ 48,418 J/mol and $k_d^0 = 0.182$, $\alpha = 1$ (first-order in CO partial pressure), $\beta = 1$ (first-order in activity), and $f_{\text{H}_2\text{O}}$ is an empirical correction factor; $f_{H_2O} = (x_{H_2O} - 1)/((1 - c) \cdot x_{H_2O} - 1)$, $(c = 0.01)$ that accounts for the inhibiting effect of water on coke formation [4].

2.3. Parametric study design

A one-at-a-time sensitivity analysis is conducted over seven parameters, each varied while the others are held at the baseline conditions: $T_{\text{in}} = 300$°C, $T_e = 300$°C, $U = 50$ W m^{-2} K^{-1}, $P_{\text{tot}} = 8$ bar, GHSV = 500 h^{-1}, $H_2/CO = 3.0$, and 0% steam. Catalyst lifetime is defined as the time for the outlet CO conversion to fall below 25% (denoted t_{25}), at which point the reactor is considered non-functional. The ranges explored are: $T_{\text{in}} = 300$–360°C, $T_e = 280$–340°C, $U = \times 0.35$–0.80 of baseline, $P_{\text{tot}} = 8$–20 bar, GHSV = 500–2000 h^{-1}, $H_2/CO = 2.0$–3.5, and steam = 0–7 mol%.

Three packing configurations are compared through their characteristic overall heat transfer coefficients: conventional cylindrical pellets ($U = 50$ W m^{-2} K^{-1}), monolithic honeycomb ($U = 150$ W m^{-2} K^{-1}), and open-cell foam ($U = 250$ W m^{-2} K^{-1}). The U values for structured supports are taken from the heat transfer literature and represent conservative estimates of the enhancement achievable with commercially available substrates.

3. Results and Discussion

3.1. Fresh-catalyst reactor profiles

On the fresh catalyst at $T_{\text{in}} = 300$°C, the reactor exhibits three characteristic zones. The kinetic zone ($z = 0$–0.03 m) is characterized by a high concentration of reactants, leading to a high reaction rate, rapid conversion increase to approximately 30%, and a consequent fast release of heat that generates a hotspot peaking at 612°C. The heat-transfer-controlled zone ($z = 0.03$–0.25 m) follows, where the depletion of reactants slows the reaction rate and the plate-cooling system brings the temperature back toward the coolant level, while conversion continues to increase. The thermodynamic zone occupies the remainder of the reactor, where equilibrium conversion (∼100%) is maintained and no further net reaction occurs.

3.2. Deactivation wave Propagation

As deactivation proceeds, the catalyst in the kinetic zone loses activity first because the extreme local temperature (612°C) drives the Boudouard coking rate to its maximum. Once the catalyst in this narrow zone is substantially deactivated, no reaction occurs there, and the reaction ignition shifts downstream into fresh catalyst. The hotspot migrates with it, forming a deactivation wave that propagates along the reactor axis. Over 20 h of operation at $T_{\text{in}} =$ 300°C, the hotspot migrates from $z \approx 0.02$ m to $z \approx 0.25$ m, while the deactivation front, where the activity drops from nearly 1 to nearly 0—

advances at the same rate.
The wave traverses the full reactor length in approximately 80–100 h. During this period, the outlet conversion remains at or near 100% because the thermodynamic zone downstream of the wave buffers the output. Only when the wave breaches this zone and erodes the remaining active catalyst does the outlet conversion begin to decline sharply, over approximately 30 h to the t_{25} threshold. This two-phase behaviour (long plateau followed by abrupt collapse) has important practical implications: the reactor appears to operate normally until the deactivation front reaches the outlet, at which point failure is rapid and difficult to reverse without catalyst replacement or regeneration.

The inlet temperature has a pronounced effect on the wave speed. Increasing T_{in} from 300 to 360°C raises the hotspot temperature throughout the reactor's life, accelerating the Boudouard rate at every axial position. The resulting t_{25} values are: 131.3 h (300°C), 99.0 h (320°C), 74.7 h (340°C), and 54.5 h (360°C)—a 58% reduction over a 60°C range.

The hotspot peak also evolves during propagation. At $t = 0$ h it reaches 612°C at $z \approx 0.02$ m; as the wave advances, the hotspot intensity decreases slightly (to approximately 580–590°C by $t = 50$ h) as the front encounters catalyst not yet preheated by the reaction, reflecting a self-decelerating mechanism. However, this deceleration is insufficient to arrest the wave: once initiated, the front propagates irreversibly through the entire reactor. The activity profile $a(z)$ at intermediate times shows a characteristic sigmoid shape, with a transition zone of 5–10 cm separating the fully deactivated upstream section ($a \approx 0$) from the still-active downstream ($a \approx 1$).

3.3. Parametric sensitivity Summary

Table 1: Parametric sensitivity: catalyst lifetime t_{25} at minimal and extreme values of each parameter.

Parameter	**Range**	t_{25} **min**	t_{25} **max**	**Factor**
T_{in}	300–360°C	54.5	131.3	2.4×
T_e	280–340°C	129.3	137.4	1.06×
U	×0.35–0.80	18.2	125.3	6.9×
P_{tot}	8–20 bar	50.5	131.3	2.6×
GHSV	500–2k h^{-1}	12.1	131.3	10.8×
H_2/CO	2.0–3.5	84.8	169.7	2.0×
Steam	0–7 mol%	131.3	171.7	1.3×

The sensitivity analysis yields a clear summary (Table 1). GHSV and U dominate the landscape. Quadrupling the GHSV from 500 to 2000 h^{-1} shortens t_{25} by a factor of 10.8× (131.3 → 12.1 h) because the higher gas velocity extends the CO-rich reactive zone over the entire bed, eliminating the thermodynamic buffer zone and exposing all catalyst to simultaneous coking. The increased throughput also delivers more CO per unit time, raising the local Boudouard driving force at every axial position. Reducing U to 0.35× baseline collapses t_{25} to 18.2 h as the intensified hotspot exponentially accelerates the Boudouard rate through the Arrhenius term.
Total pressure exerts a detrimental effect (−62% from 8 to 20 bar) because the CO partial pressure, the driving force for Boudouard coking, scales linearly with P_{tot} at constant mole fraction, and this effect overwhelms the modest equilibrium shift benefit. The inlet temperature reduces t_{25} by 58% over the 300–360°C range, consistent with the Arrhenius sensitivity of the deactivation kinetics.
Feed composition offers effective and low-cost mitigation. Increasing H_2/CO from 2.0 to 3.5 doubles t_{25} (84.8 → 169.7 h, +100%) by diluting the inlet CO concentration and accelerating its consumption via the forward methanation reaction, which shrinks the reactive zone. Steam co-feeding at 7 mol% extends t_{25} by 31% (131.3 → 171.7 h) through the f_{H_2O} inhibition factor in the deactivation rate expression, which suppresses the local coking rate. The coolant temperature has a negligible effect (∼5%), as the hotspot magnitude was found to be governed primarily by the inlet temperature and kinetics rather than by the downstream cooling rate.

3.4. Configuration comparison and hotspot suppression

Table 2: Configuration comparison: hotspot suppression and lifetime extension.

Metric	Pellets	Monolith	Foam
U [W m^{-2} K^{-1}]	50	150	250
$T_{\max}$ [°C]	612	570	539
ΔT vs. pellets [°C]	—	−42	−73
t_{25} [h]	126.3	343.4	459.6
Lifetime factor	1× (ref.)	2.72×	3.64×

The open-cell foam achieves $t_{25} = 459.6$ h, a 3.64-fold improvement over the packed-bed baseline (Table 2), driven by two complementary mechanisms. First, the 73°C hotspot reduction (612 → 539°C) decreases the local Arrhenius deactivation rate at the hotspot by a factor of 25–35. To quantify this: at 612°C (885 K) the Arrhenius factor $\exp(-E_d/RT)$ is approximately 25–35 times larger than at 539°C (812 K), given $E_d = 48{,}418$ J/mol. This exponential sensitivity is the fundamental reason why even a moderate hotspot reduction translates into a large lifetime gain. The Arrhenius factor at 570°C (monolith hotspot) is approximately 8–12 times that at 539°C, which is consistent with the monolith achieving 75% of the foam's lifetime improvement.

Second, analysis of the temperature profile evolution at $t = 0$, 10, and 20 h reveals that the hotspot in the foam configuration is essentially pinned near the reactor inlet ($z < 0.05$ m), with the three time-snapshots nearly overlapping. In contrast, the packed-bed hotspot migrates from $z \approx 0.02$ m to $z \approx 0.25$ m within the same 20 h period, sweeping through 25% of the reactor length and deactivating catalyst over that entire volume. The foam's three-dimensional strut network promotes radial heat transfer to the cooled walls, confining the thermal footprint to less than 5 cm and preventing the deactivation wave from propagating.

The monolith achieves an intermediate improvement (2.72×, $t_{25} = 343.4$ h) with a 42°C hotspot reduction (612 → 570°C). Its continuous ceramic walls provide axial heat conduction paths, effective but less isotropic than the foam's strut network. The overall 3.64× improvement is lower than the local 25–35× rate reduction because deactivation is volume-averaged: in cooler downstream sections, coking rates are already low regardless of configuration. In the monolith, continuous walls act as axial conduction fins; in the foam, the three-dimensional strut network enhances radial convective transfer isotropically, explaining the additional 31°C reduction and 1.34× further lifetime gain.

3.5. Activity profile dynamics and parameter interactions

The temporal evolution of the axial activity profile $a(z,t)$ further distinguishes the three configurations. In the packed bed, the activity profile at intermediate times exhibits a characteristic sigmoid shape: a sharp transition zone (width ≈ 5–10 cm) separates a fully deactivated upstream section ($a \approx 0$) from the still-active downstream section ($a \approx 1$). This front is driven by the hotspot, which locally accelerates coking to completion before migrating downstream. The practical consequence is binary output behaviour: the reactor operates at near-full conversion during the plateau, then collapses abruptly within approximately 30 h once the front reaches the outlet.

In the foam configuration, by contrast, the suppressed hotspot produces a more homogeneous temperature field, and the activity declines uniformly across the bed. The outlet conversion decreases gradually from the start of operation, providing earlier warning of degradation over a much longer operational window. The monolith exhibits intermediate behaviour: a discernible front exists but migrates more slowly, with a broader transition zone (≈15–20 cm), consistent with the 42°C hotspot reduction that moderates but does not eliminate the exponential temperature sensitivity of the Boudouard rate.

The benefit of structured supports is most pronounced at low GHSV values, where the thermodynamic buffer zone exists and the hotspot is localised. At GHSV = 2000 h^{-1}, the reactive zone extends over the entire reactor regardless of U, and the advantage of enhanced cooling is diminished because coking occurs everywhere simultaneously. Structured supports should therefore

be paired with moderate space velocities to maximize their benefit.
Similarly, the steam co-feeding strategy interacts with the temperature profile: at 300°C the full 31% benefit of 7 mol% steam is realized, whereas at 360°C the water-gas shift equilibrium partially counteracts the inhibiting effect. The combination of foam supports (hotspot suppression), moderate steam addition (chemical inhibition), and low inlet temperature (Arrhenius-limited kinetics) therefore represents the most effective strategy for catalyst lifetime maximization.

4. Conclusions

This thesis demonstrates that the pseudodynamic modelling framework of Pappagallo et al. [4] can be extended to a comprehensive parametric optimization tool for fixed-bed CO methanation reactors subject to Boudouard coking. The principal scientific contributions and engineering implications are summarized below.
Thermal management dominates catalyst lifetime. The overall heat transfer coefficient U and the inlet temperature T_{in} are the two most influential parameters, confirming that hotspot suppression—rather than feed composition or operating pressure—is the primary design objective for long-life methanation reactors. The Arrhenius coupling between the hotspot temperature and the Boudouard deactivation kinetics (E_d = 48,418 J/mol) amplifies even modest thermal improvements into large lifetime gains.

Structured catalyst supports offer transformative lifetime extension. Open-cell foam ($U = 250\ \text{W m}^{-2}\,\text{K}^{-1}$) achieves a 3.64-fold improvement over the conventional packed bed (459.6 vs. 126.3 h), driven by a 73°C hotspot reduction and near-complete suppression of hotspot migration. The monolithic honeycomb (2.72×, 343.4 h) provides a cost-effective and industrially proven alternative suitable for retrofitting existing reactors.

Feed composition strategies provide complementary benefits. Steam co-feeding at 7 mol% (+31%) and moderately excess hydrogen ($H_2/CO = 3.5$, +100%) each extend catalyst lifetime independently of the packing configuration. These low-cost operational changes can be combined with structured supports for cumulative benefit. Conversely, high total pressure (−62% at 20 bar) and high GHSV (−90% at 2000 h^{-1}) are strongly detrimental and must be minimized.

Pseudodynamic framework validated as a practical design tool. The computational efficiency of the pseudodynamic approach, requiring only the integration of a single ODE coupled with successive steady-state reactor solves—makes it well-suited for multi-parameter optimization studies. The extension from the original four-temperature study [4] to a seven-parameter space with three catalyst configurations demonstrates the modularity and versatility of the framework for reactor-scale deactivation analysis in CO methanation systems.

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