Group Project - CLL 222

Modeling Oxide Oxidation: Microkinetic vs. PSSA vs. QEA

Submitted to:

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1   Acknowledgement

We would like to express our sincere gratitude to our course instructor Divesh Bhatia for providing valuable guidance, support, and resources throughout this project. Their insights on reaction kinetics and catalytic modeling greatly helped us understand the differences between microkinetic, pseudo-steady-state, and quasi-equilibrium approaches.

We also thank our teaching assistants and department staff for their continuous help during discussions and laboratory sessions. We are grateful to our teammates for their equal contribution, coordination, and consistent effort in completing this project on time. Finally, we acknowledge the support of our institute for providing the academic environment and facilities required for this work.

2 Team Contribution

This section outlines the individual contributions of each member involved in the project. The work was carried out collaboratively, and each member played an important role in completing the modelling, analysis, coding, and documentation. The specific contributions are detailed below.

Shobhit Kumar (2023CH70769)

I implemented the complete computational workflow for this project, including formulation and solution of the microkinetic, models using Python-based ODE solvers. I generated all concentration, surface-coverage, and rate plots, and designed the overall visualization strategy—for example, selecting which variables to plot and comparing rate vs. pressure of reactants and products to determine apparent reaction orders. I also handled model setup, numerical integration, and result and discussion for all three approaches.

Paras Kansal (2023CH10196)

I conducted the literature review on the Quasi-Equilibrium Approximation (QEA) and the Pseudo Steady State Approximation (PSSA), studied their modeling frameworks, and implemented these assumptions in the kinetic analysis. I worked on the problem objectives related to understanding how these approximations simplify the microkinetic mechanism. Additionally, I generated the corresponding graphs and plots for these models and contributed to interpreting their results for the comparative study.

Nishka Murarka (203CH71178)

My contribution focused on studying and modeling the Pseudo–Steady–State (PSS) and Quasi Equilibrium (QE) approximations for catalytic reactions. After deriving the governing equations, implemented them in Python to simulate reaction rates. I generated corresponding plots that enabled a clear visual comparison with the full microkinetic model. This helped us understand how the approximations simplify the system and allowed assessing their accuracy.

Tushar Gupta (2023CH10718)

My major contribution to this project involved both writing and research-related tasks. I also compiled, organized, and formatted all references used in the report, maintaining consistency with academic citation standards. In addition, I assisted in collecting and formatting the dataset required for the analysis, ensuring that all relevant data were properly compiled and ready for use. Through these contributions, I helped ensure the completeness, clarity, and coherence of the final project report.

3 Abstract

This project presents a comprehensive comparative kinetic analysis of Carbon Monoxide (CO) oxidation on a catalytic surface, a mechanism critical to emission control technology. The study rigorously evaluates three distinct modeling methodologies applied to the Langmuir–Hinshelwood mechanism: Microkinetic Modeling, the Pseudo-Steady-State Approximation (PSSA), and the Quasi-Equilibrium Approximation (QEA).

The Microkinetic Model provides the most fundamental, time-dependent description by numerically solving the full system of Ordinary Differential Equations (ODEs) for all species coverages. The PSS (Pseudo-Steady State) approximation simplifies this by assuming that reactive surface intermediates exist in very small concentrations and that their rates of formation and consumption nearly balance, i.e., $\frac{d\theta_i}{dt} \approx 0$. In contrast, the QEA (assuming the surface reaction is the Rate-Determining Step, RDS) yields a simplified, closed-form analytical rate law preferred for industrial reactor design.

This comparison provides a basis for examining how microkinetic, PSS, and QEA treatments shape the development of rate expressions for CO oxidation, offering a structured view of their respective roles in catalytic reaction modelling.
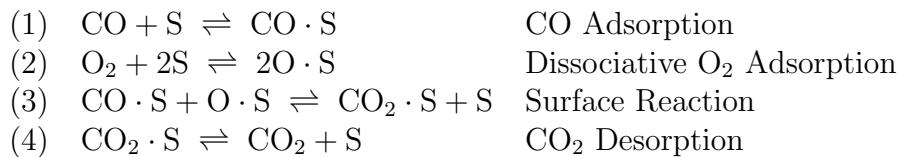
4 Introduction

4.1 Background and Motivation

The catalytic oxidation of Carbon Monoxide (CO) to Carbon Dioxide (CO_2) is vital in environmental and industrial engineering. It is best known for its use in automobile catalytic converters to meet strict emission standards, but it is equally important in industrial flue gas treatment and hydrogen fuel cells, where trace CO must be removed to prevent catalyst poisoning. This reaction also underpins CO detection in safety sensors and life-support systems used in mines, submarines, and spacecraft. Additionally, CO-rich off-gases are sometimes oxidized to recover heat energy, and the reaction itself is widely used as a model system to test and develop new catalysts.

Predictive models like PSSA and QEA must be derived from the molecular-level steps — a methodology known as *microkinetic modeling*. Our motivation is to compare this rigorous approach with simplified approximations to understand the balance between computational accuracy and analytical simplicity.

The mechanism under study is the Langmuir–Hinshelwood (L–H) mechanism:

$$
\begin{array}{lll}
(1) & CO + S \rightleftharpoons CO \cdot S & \text{CO Adsorption} \\
(2) & O_2 + 2S \rightleftharpoons 2O \cdot S & \text{Dissociative } O_2 \text{ Adsorption} \\
(3) & CO \cdot S + O \cdot S \rightleftharpoons CO_2 \cdot S + S & \text{Surface Reaction} \\
(4) & CO_2 \cdot S \rightleftharpoons CO_2 + S & \text{CO}_2 \text{ Desorption}
\end{array}
$$

4.2 Problem Statement

Modeling the CO oxidation mechanism requires accounting for three transient surface intermediates: CO·S, O·S, and CO_2·S. This leads to a highly coupled system with significant analytical and numerical complexity. The challenge lies in managing this complexity across three levels of kinetic rigor:

- **Microkinetic Modeling (Full ODE System):** The system is described by a set of Ordinary Differential Equations (ODEs) governing surface coverages. While providing the most accurate, time-dependent description, this method requires stiff numerical solvers (e.g., BDF) and is computationally intensive.

- **Full Pseudo-Steady-State Approximation (PSSA):** Setting $d\theta_i/dt \approx 0$ for all intermediates yields a system of nonlinear algebraic equations. For CO oxidation, this system becomes analytically insoluble, preventing derivation of a closed-form rate law.

- **Quasi-Equilibrium Approximation (QEA) / Rate-Determining Step (RDS):** This industrially preferred simplification assumes that steps preceding the surface reaction are in quasi-equilibrium. Only under this assumption does the mechanism yield a usable explicit analytical rate expression.

4.3 Project Objectives

The primary objectives of this project are:

1. **Establish the Microkinetic Benchmark:** Formulate the complete set of ODEs describing surface species coverages and reaction rates.

2. **Evaluate Analytical Limits of PSSA:** Derive the full nonlinear algebraic equations from the PSSA and demonstrate their analytical intractability.

3. **Derive and Validate the Practical QEA Model:** Apply the QEA/RDS assumption to obtain the explicit Langmuir–Hinshelwood rate expression and interpret its kinetic implications.

4. **Comparative Analysis:** Contrast the computational effort and outputs of all three methodologies to justify why the QEA/RDS model remains the dominant industrial tool.

4.4 Github Repository
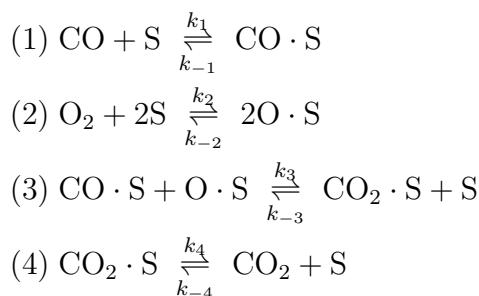
The coding part of this project, including Python scripts for solving ODEs, microkinetic modeling, PSSA and QE analysis, and plot generation, was developed as part of this work. All scripts and related files are available in the project repository: GitHub Repository . The repository contains the full code, data, and instructions to reproduce the results and figures presented in this report.

5 Modelling Methodology

5.1 Microkinetic Modelling

Microkinetic modeling represents a catalytic reaction as a sequence of elementary steps, each described by its own thermodynamically consistent forward and reverse rate expressions. Adsorption, surface reactions, and desorption are treated explicitly rather than being lumped into a single overall rate law. These individual rate equations are solved simultaneously to determine surface coverages and the resulting reaction rate. This step-resolved approach makes the reaction pathway, kinetic contributions, and rate-controlling steps directly visible. Consequently, microkinetic modeling provides a structured and technically rigorous framework for analysing catalytic mechanisms and comparing different modeling methodologies.

5.1.1 Reaction Mechanism and Elementary Step Rates The Langmuir–Hinshelwood mechanism for CO oxidation consists of the following elementary steps:

$$(1)\ CO + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO \cdot S$$

$$(2)\ O_2 + 2S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2O \cdot S$$

$$(3)\ CO \cdot S + O \cdot S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CO_2 \cdot S + S$$

$$(4)\ CO_2 \cdot S \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} CO_2 + S$$

Elementary Step Rates

$$r_1 = k_1 C_T P_{CO}\, \theta_v - k_{-1} C_T \theta_{CO \cdot S},$$
$$r_2 = k_2 C_T P_{O_2}\, \theta_v^2 - k_{-2} C_T \theta_{O \cdot S}^2,$$
$$r_3 = k_3 C_T \theta_{CO \cdot S} \theta_{O \cdot S} - k_{-3} C_T \theta_{CO_2 \cdot S} \theta_v,$$
$$r_4 = k_4 C_T \theta_{CO_2 \cdot S} - k_{-4} C_T P_{CO_2}\, \theta_v.$$

5.1.2 Governing Differential Equations

$$\frac{d\theta_{CO \cdot S}}{dt} = r_1 - r_3,$$
$$\frac{d\theta_{O \cdot S}}{dt} = 2r_2 - r_3,$$
$$\frac{d\theta_{CO_2 \cdot S}}{dt} = r_3 - r_4.$$

Gas-phase ODEs (for a batch reactor):

$$\frac{d[CO]}{dt} = -r_1, \qquad \frac{d[O_2]}{dt} = -r_2, \qquad \frac{d[CO_2]}{dt} = r_4.$$

5.1.3 Site Balance

$$\theta_{\text{CO·S}} + \theta_{\text{O·S}} + \theta_{\text{CO}_2\text{·S}} + \theta_v = 1.$$

Thus,

$$\theta_v = 1 - \left(\theta_{\text{CO·S}} + \theta_{\text{O·S}} + \theta_{\text{CO}_2\text{·S}}\right).$$

5.1.4 Overall Reaction Rate   The overall reaction rate (Rate) is the instantaneous volumetric rate of CO_2 formation via desorption (Step 4):

$$\boxed{\text{Rate}(t) = r_4 = k_4 C_T \theta_{\text{CO}_2\text{·S}}(t) - k_{-4} C_T P_{\text{CO}_2}(t)\, \theta_v(t)}$$

5.1.5 Solution Methodology   The Microkinetic Model requires numerical integration of the three coupled ODEs (after substituting the full rate expressions r_1–r_4) to obtain the dynamic solution $\theta_i(t)$. This yields the full transient coverage profiles and provides the most accurate benchmark for the overall reaction rate $r(t)$.

5.2   Pseudo–Steady–State Approximation (PSSA)

The Pseudo–Steady–State Approximation (PSSA) simplifies catalytic reaction analysis by assuming that the concentrations of highly reactive surface intermediates remain effectively constant over time. Instead of tracking their rapid transient behavior, the time derivatives of these intermediates are set to zero, reducing the system of differential equations from the microkinetic model to a set of algebraic relations. This allows surface coverages and reaction rates to be determined without solving the full dynamic system. By removing short-lived variables while preserving key kinetic interactions, PSSA provides a faster way to analyze catalytic reactions while still capturing the key mechanisms, making it easier to understand complex pathways and find rate-limiting steps.

5.2.1 PSSA Assumption and Governing Algebraic Equations   Under PSSA, the fractional coverages of all adsorbed intermediates satisfy:

$$\frac{d\theta_{\text{CO·S}}}{dt} \approx 0, \qquad \frac{d\theta_{\text{O·S}}}{dt} \approx 0, \qquad \frac{d\theta_{\text{CO}_2\text{·S}}}{dt} \approx 0.$$

Using the Microkinetic ODEs:

$$\frac{d\theta_{\text{CO·S}}}{dt} = r_1 - r_3, \qquad \frac{d\theta_{\text{O·S}}}{dt} = 2r_2 - r_3, \qquad \frac{d\theta_{\text{CO}_2\text{·S}}}{dt} = r_3 - r_4,$$

the PSSA gives the following algebraic relations:

$$\text{PSSA Eq. (1):} \quad r_1 = r_3,$$
$$\text{PSSA Eq. (2):} \quad 2r_2 = r_3,$$
$$\text{PSSA Eq. (3):} \quad r_3 = r_4.$$

5.2.2 Intractability of the Full PSSA System To obtain an explicit analytical rate law, the three PSSA equations must be solved together with the surface site balance:

$$\theta_{\text{CO·S}} + \theta_{\text{O·S}} + \theta_{\text{CO}_2\text{·S}} + \theta_v = 1.$$

The unknowns are:

$$\theta_{\text{CO·S}}, \ \theta_{\text{O·S}}, \ \theta_{\text{CO}_2\text{·S}}, \ \theta_v.$$

Substituting the full rate expressions:

$$r_1 = k_1 C_T P_{\text{CO}} \, \theta_v - k_{-1} C_T \, \theta_{\text{CO·S}},$$
$$r_2 = k_2 C_T P_{\text{O}_2} \, \theta_v^2 - k_{-2} C_T \, \theta_{\text{O·S}}^2,$$
$$r_3 = k_3 C_T \, \theta_{\text{CO·S}} \, \theta_{\text{O·S}} - k_{-3} C_T \, \theta_{\text{CO}_2\text{·S}} \, \theta_v,$$
$$r_4 = k_4 C_T \, \theta_{\text{CO}_2\text{·S}} - k_{-4} C_T P_{\text{CO}_2} \, \theta_v,$$

the PSSA relations (e.g., $r_3 = r_4$) give highly nonlinear equations such as:

$$k_3 C_T \theta_{\text{CO·S}} \theta_{\text{O·S}} - k_{-3} C_T \theta_{\text{CO}_2\text{·S}} \theta_v = k_4 C_T \theta_{\text{CO}_2\text{·S}} - k_{-4} C_T P_{\text{CO}_2} \theta_v.$$

These contain nonlinear coupling terms:

$$\theta_{\text{CO·S}} \theta_{\text{O·S}}, \quad \theta_{\text{O·S}}^2, \quad \theta_v^2,$$

making the full algebraic system analytically unsolvable in closed form.

5.2.3 Conclusion on PSSA

- **PSSA fails to simplify the mechanism:** although the ODEs are removed, the resulting algebraic equations are too nonlinear to solve explicitly for the coverages.

- **Numerical solution is unavoidable:** the system must be solved using iterative nonlinear solvers such as Newton–Raphson.

- **Justification for QEA:** because PSSA cannot produce a closed–form rate law, catalytic kinetics relies on the Quasi–Equilibrium Approximation (QEA) along with the Rate–Determining Step (RDS) assumption to obtain an analytical Langmuir–Hinshelwood rate expression.

5.3   Quasi–Equilibrium Approximation (QEA)
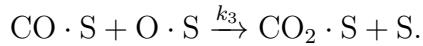
The Quasi–Equilibrium Approximation (QEA) simplifies the treatment of catalytic mechanisms by assuming that all fast adsorption and desorption steps rapidly reach equilibrium before the slower rate-determining step (RDS) proceeds. Under this assumption, the forward and reverse rates of these fast steps are balanced, allowing their surface coverages to be expressed using equilibrium

constants rather than differential equations. This converts a portion of the microkinetic ODE system into analytical algebraic relationships, enabling the derivation of an explicit rate law without solving the full dynamic model. By separating fast equilibrated steps from the slow controlling step, QEA provides a structured and physically meaningful way to capture essential kinetics while reducing computational complexity.

5.3.1 QEA Assumptions and RDS Identification For the CO oxidation mechanism:

- **Fast equilibrium steps:** CO adsorption (Step 1), O_2 dissociative adsorption (Step 2), and CO_2 desorption (Step 4).

- **Slow irreversible(assumption) RDS:** The surface reaction (Step 3):

$$\text{CO} \cdot \text{S} + \text{O} \cdot \text{S} \xrightarrow{k_3} \text{CO}_2 \cdot \text{S} + \text{S}.$$

Thus, the rate depends only on the forward rate of Step 3:

$$\text{Rate} = r_3 = k_3 \, \theta_{\text{CO·S}} \, \theta_{\text{O·S}}. \tag{1}$$

5.3.2 Equilibrium Coverage Expressions The equilibrium constants for the fast steps give:

$$\theta_{\text{CO·S}} = K_{\text{CO}} \, P_{\text{CO}} \, \theta_v, \tag{2}$$

$$\theta_{\text{O·S}} = \sqrt{K_{\text{O}_2} P_{\text{O}_2}} \, \theta_v, \tag{3}$$

$$\theta_{\text{CO}_2 \cdot \text{S}} = \frac{P_{\text{CO}_2}}{K_{\text{CO}_2}} \, \theta_v. \tag{4}$$

5.3.3 Vacant Site Coverage θ_v The site balance is:

$$\theta_{\text{CO·S}} + \theta_{\text{O·S}} + \theta_{\text{CO}_2 \cdot \text{S}} + \theta_v = 1. \tag{5}$$

Substituting (2)–(4):

$$\theta_v \left(1 + K_{\text{CO}} P_{\text{CO}} + \sqrt{K_{\text{O}_2} P_{\text{O}_2}} + \frac{P_{\text{CO}_2}}{K_{\text{CO}_2}} \right) = 1.$$

Thus,

$$\boxed{\theta_v = \frac{1}{1 + K_{\text{CO}} P_{\text{CO}} + \sqrt{K_{\text{O}_2} P_{\text{O}_2}} + \frac{P_{\text{CO}_2}}{K_{\text{CO}_2}}}} \tag{6}$$

5.3.4 Final QEA Analytical Rate Law   Substituting (2), (3), and (6) into (1):

$$\text{Rate} = k_3 \left(K_{\text{CO}} P_{\text{CO}} \theta_v \right) \left(\sqrt{K_{\text{O}_2} P_{\text{O}_2}} \, \theta_v \right),$$

$$\text{Rate} = \left[k_3 K_{\text{CO}} \sqrt{K_{\text{O}_2}} \, P_{\text{CO}} \sqrt{P_{\text{O}_2}} \right] \theta_v^2.$$

Final QEA rate expression:

$$\text{Rate}_{\text{QEA}} = \frac{k_3 K_{\text{CO}} \sqrt{K_{\text{O}_2}} \, P_{\text{CO}} \sqrt{P_{\text{O}_2}}}{\left(1 + K_{\text{CO}} P_{\text{CO}} + \sqrt{K_{\text{O}_2} P_{\text{O}_2}} + \frac{P_{\text{CO}_2}}{K_{\text{CO}_2}} \right)^2}$$

This provides the explicit Langmuir–Hinshelwood rate law under the QEA assumption.

6   Results and Discussion

Based on the provided plots for the CO oxidation reaction, the concentration profiles figures 1,2 and 3 show that while all models eventually reach a final state where reactants are consumed and product is formed, the microkinetic model exhibits a significantly slower overall reaction rate compared to the PSSA and QE models (note the larger reactant consumption in the PSSA/QE plots). In the PSSA and QE models, CO and O_2 concentrations drop rapidly and CO_2 concentration rises quickly, stabilizing within ≈ 0.015 s. The microkinetic model, however, shows a more gradual change across the entire time frame. This suggests that the simplified approximations (PSSA and QE) might overpredict the speed of the macroscopic reaction compared to the full microkinetic description, which includes a more detailed and slower adjustment of the gas-phase species.
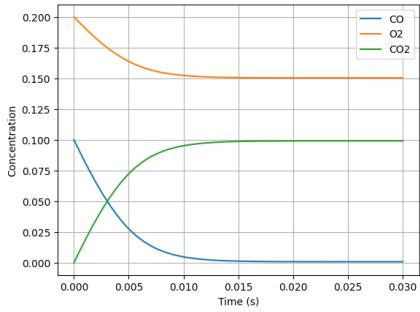
Figure 1: PSSA concentration profile
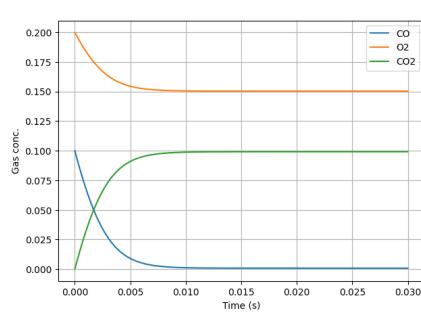
Figure 2: QE concentration profile
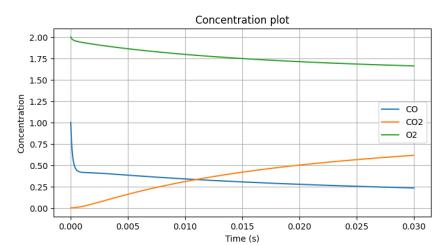
Figure 3: Microkinetic concentration profile

The {surface coverage profiles} in Figures 4, 5, and 6 confirm the complex transient behavior captured by the full model. The {microkinetic coverages} show a sharp, non-monotonic evolution: θ_{CO} quickly rises before decaying, while θ_V (empty sites) drops sharply and then partially recovers, mirroring the rate spike. Conversely, the {PSSA and QEA coverages} exhibit a simple, monotonic evolution: θ_{CO} decays monotonically, θ_O rises, and θ_V increases smoothly, all approaching their final steady-state values. All three models converge to similar steady-state coverages, with empty sites (θ_V) being the dominant surface species (around 80%), confirming that the {approximations accurately predict the final state} but {miss the highly dynamic evolution} of the surface required to reach that state.
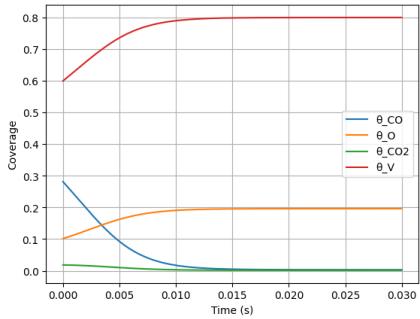

Figure 4: PSSA surface coverage
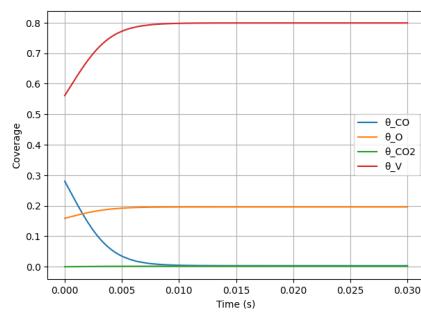

Figure 5: QE surface coverage
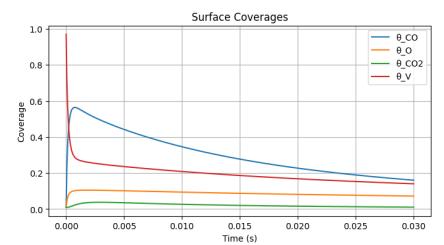
Figure 6: Microkinetic surface coverage

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The reaction rate profiles figure 7,8 and 9 reveal a critical difference in the predicted transient behavior. The microkinetic rate exhibits a sharp, non-monotonic peak (around 38) immediately after $t = 0$, followed by a steady decay. This rate spike is characteristic of a reaction where a necessary surface intermediate quickly accumulates before reacting. In contrast, the PSSA rate shows a smoother, monotonic decay, starting from a lower value (around 18) and missing the initial rate spike entirely, indicating that the PSSA assumption of zero accumulation rate for surface species is invalid during this transient ($\partial\theta_i/\partial t \neq 0$). The QE rate plot is similar to PSSA but starts at the high peak value (around 35), still failing to capture the fast rise and decay seen in the microkinetic model, confirming that both approximations are inaccurate in describing the crucial initial dynamic phase.
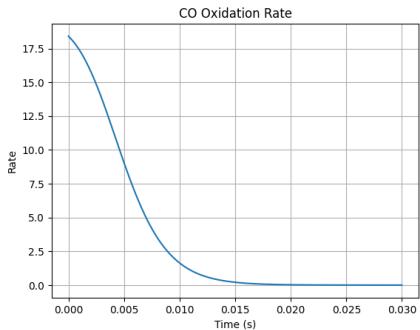

Figure 7: PSSA rate
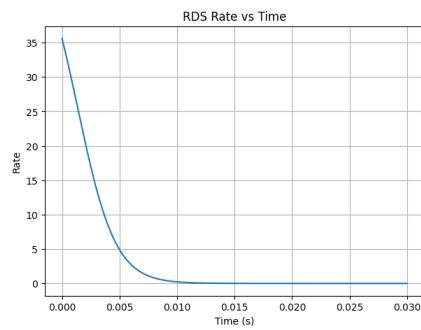
Figure 8: QE rate
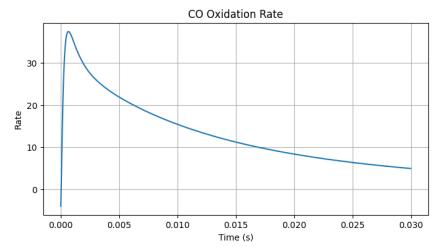
Figure 9: Microkinetic rate

The log(rate) vs. log(CO) plots figure 10, 11 and 12 show the reaction order with respect to CO is always positive but not constant, confirming it is an essential reactant. The Microkinetic model exhibits the most complex behavior, where the slope (reaction order) decreases significantly as log(CO) increases, showing a clear plateau and subsequent sharp drop at the highest CO concentration (around log(CO) = −0.8). This indicates that the reaction is inhibited by high CO coverage, which is a hallmark of the Langmuir-Hinshelwood mechanism where CO blocks sites for O_2 adsorption. In contrast, the PSSA and QE models predict a simpler, consistently increasing log(rate) with increasing log(CO), suggesting they fail to capture the CO inhibition effect, particularly at higher concentrations (less negative log(CO) values), where the microkinetic rate starts to drop.
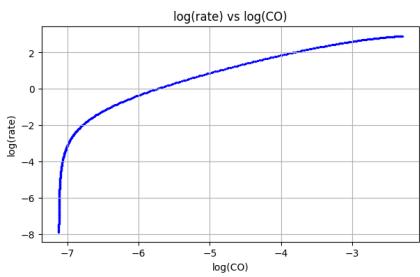

Figure 10: PSSA rate and P_{CO}
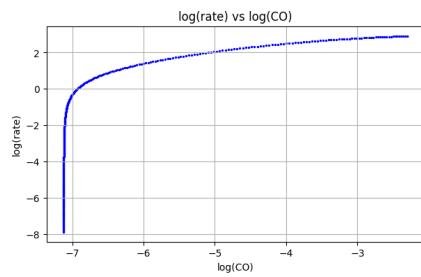
Figure 11: QE rate and P_{CO}
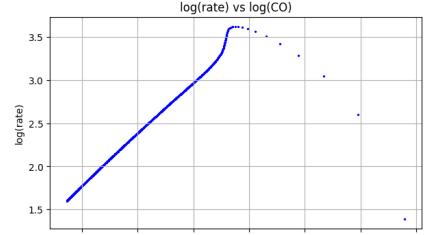
Figure 12: Microkinetic rate and P_{CO}

The plots for log(rate) vs. log(O_2) figure 13, 14 and 15 consistently show a positive reaction order with respect to O_2 across all models, indicating that O_2 is a limiting reactant in the studied regime. The Microkinetic model shows a complex, non-linear relationship, with a positive slope that slightly increases before peaking and then dropping sharply at the highest log(O_2) value (around 0.67), suggesting that the rate is maximized at an intermediate concentration ratio of CO to O_2. The PSSA and QE models are nearly identical and much simpler, showing the log(rate) rapidly leveling off to a constant value as log(O_2) increases (i.e., the rate becomes nearly zero-order with respect to O_2 at high concentrations, above log(O_2) ≈ -1.75). This suggests that the simpler models transition to an O_2-saturated regime much earlier than the microkinetic model, where the reaction is then limited by the CO available on the surface.
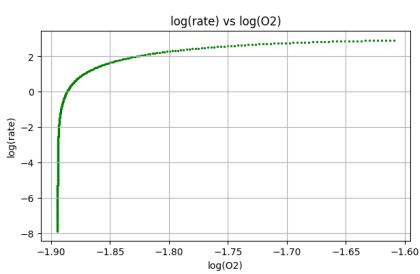

Figure 13: PSSA rate and P_{O2}
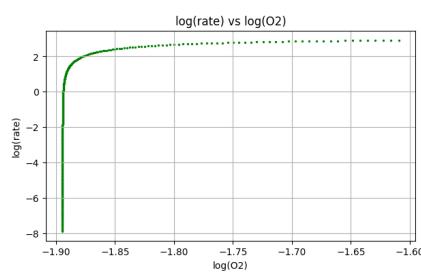
Figure 14: QE rate and P_{O2}
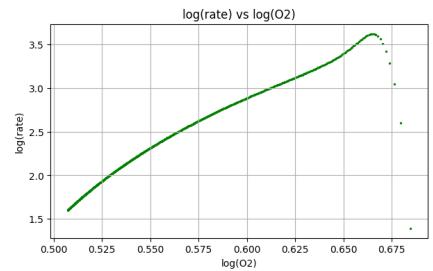
Figure 15: Microkinetic rate and P_{O2}

The log(rate) vs. log(CO_2) plots figure 16, 17 and 18 display a characteristic negative reaction order with respect to CO_2 at high product concentrations (less negative log(CO_2) values). This effect is most pronounced near the end of the reaction, where the steep negative slope indicates product inhibition, a phenomenon where the adsorbed product (CO_2) or the reverse reaction becomes significant, slowing the forward rate. The PSSA and QE models are almost indistinguishable, showing a sharp drop in rate only at the very end (around log(CO_2) ≈ -2.5). The Microkinetic model shows this drop over a much broader range of CO_2 concentrations (starting around log(CO_2) ≈ -4.0), and the peak log(rate) is significantly higher. This difference highlights that while all models acknowledge product inhibition, the microkinetic model predicts that this inhibition begins at a lower CO_2 concentration and that the overall reaction dynamics are more sensitive to the accumulation of CO_2 throughout the process.
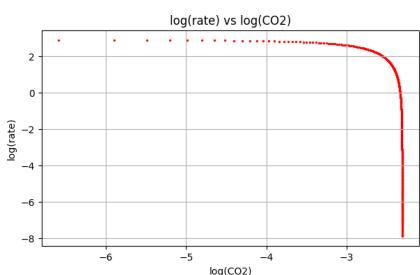

Figure 16: PSSA rate and P_{cO2}
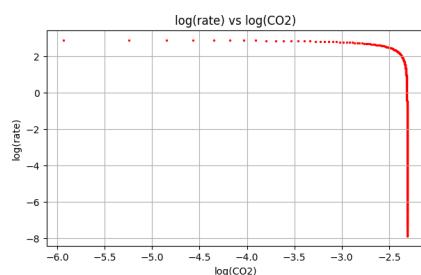
Figure 17: QE rate and P_{cO2}
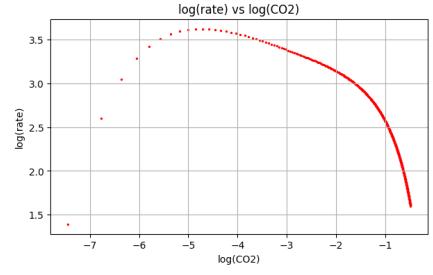
Figure 18: Microkinetic rate and P_{cO2}

7   Conclusion

In this project, we carried out a detailed comparative study of three kinetic modeling frameworks: Microkinetic Modeling, the Pseudo–Steady–State Approximation (PSSA), and the Quasi-Equilibrium Approximation (QEA) for the Langmuir–Hinshelwood mechanism of CO oxidation. The microkinetic model provided the most rigorous description by capturing the full transient evolution of surface and gas-phase species, revealing complex coverage behavior that simplified models cannot represent. However, its computational cost and the requirement for stiff ODE solvers make it less convenient for engineering calculations.

The PSSA approach simplified the dynamic equations but resulted in a set of highly nonlinear algebraic relationships that proved analytically intractable. Although PSSA predicts rapid adjustment to steady state and yields reasonable final coverages, it cannot provide a closed-form rate expression, limiting its applicability in reactor modeling and design.

The QEA model, based on assuming fast adsorption–desorption equilibria and a slow rate-determining surface reaction, produced an explicit Langmuir–Hinshelwood rate law. This analytical tractability makes QEA the most practical tool for industrial kinetic analysis, eve though it often predicts reaction rates that are higher than real values and overlooks the fine time-dependent changes occurring on the catalyst surface, leading to a loss of detailed transient behavior.

Overall, the results show that microkinetic modeling is essential for mechanistic understanding, PSSA offers limited simplification, and QEA remains the preferred method for engineering applications. The study highlights the trade-off between accuracy and usability, emphasizing the need to select a kinetic modeling approach based on the specific objectives of analysis or design.

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