A Comparative Thermodynamic and Kinetic Analysis of Methane Tri-Reforming for Syngas Production: A Process Simulation Approach

Análisis termodinámico y cinético comparativo del tri-reformado de metano para la producción de gas de síntesis: un enfoque de simulación de procesos

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Abstract

The growing concentration of greenhouse gases, primarily methane (CH_4) and carbon dioxide (CO_2), underscores the need for advanced carbon capture and utilization (CCU) technologies. Methane tri-reforming (TRM) has emerged as a highly promising pathway for the valorizitation of these gases, converting them into syngas (a mixture of H_2/CO), which serves a critical feedstock for the chemical industry. This study develops and applies a comprehensive process simulation framework to systematically evaluate the TRM process, addressing a notable gap in the literature regarding the rigorous comparison between thermodynamic limits and actual kinetic performance under different feed compositions. Using the *DWSIM* process simulator (version 8.1.2), a comparative analysis was conducted employing two distinct reactor models: a Gibbs reactor model to determine thermodynamic equilibrium limits and a kinetic Plug Flow Reactor (PFR) model to assess performance under practical conditions. The investigation evaluated three different feed compositions, varying the molar ratios, with the objective of identifying optimality criteria based on: (1) maximum combined conversion of CH_4 and CO_2, (2) suppression of coke formation, (3) efficient production of adjustable syngas, and (4) favorable energy balance. The thermodynamic analysis identified an optimal operating window between 800 K and 900 K at atmospheric pressure, where reactant conversions are maximized and secondary coke-forming reactions are suppressed. The kinetic analysis revealed that an ideal feed composition (molar fractions of: CH_4= 0,545, CO_2 =0,182, H_2O =0,091) achieves a methane conversion of 33,0% and produces syngas with an H_2/CO molar ratio of 3,0 at 800 K, representing

the best compromise between conversion and selectivity. Finally, thermal and composition profiles along the reactor were evaluated, demonstrating syngas formation and the accelerated methane consumption during the tri-reforming process. This work provides a robust computational methodology for optimizing TRM feed conditions and producing syngas with tunable compositions, offering valuable insights for the conceptual design and scale-up of reactors for sustainable chemical production.

Keywords: *DWSIM*, chemical equilibrium, catalytic reactor, computational simulation, methane tri-reforming, process simulation, reaction kinetics, syngas, thermodynamic analysis.

Resumen

La creciente concentración de gases de efecto invernadero, principalmente metano (CH_4) y dióxido de carbono (CO_2), resalta la necesidad de tecnologías avanzadas de captura y utilización de carbono (CCU). El reformado triple de metano (TRM, por sus siglas en inglés) ha surgido como una vía muy prometedora para valorizar estos gases, convirtiéndolos en gas de síntesis (syngas, una mezcla de H_2/CO), una materia prima crítica para la industria química. Este estudio desarrolla y aplica un marco integral de simulación de procesos para evaluar sistemáticamente el proceso TRM, abordando la brecha existente en la literatura sobre la comparación rigurosa entre los límites termodinámicos y el rendimiento cinético real bajo diferentes composiciones de alimentación. Utilizando el simulador de procesos DWSIM (versión 8.1.2), se realizó un análisis comparativo empleando dos modelos de reactor distintos: un modelo de reactor de Gibbs para determinar los límites de equilibrio termodinámico y un modelo cinético de Reactor de Flujo Pistón (PFR) para evaluar el rendimiento en condiciones prácticas. La investigación evaluó tres composiciones de alimentación diferentes, variando las relaciones molares, con el objetivo de identificar criterios de optimalidad basados en: (1) máxima conversión conjunta de CH_4 y CO_2, (2) supresión de la formación de coque, (3) producción eficiente de syngas ajustable, y (4) balance energético favorable. El análisis termodinámico identificó una ventana de operación óptima entre 800 K y 900 K a presión atmosférica, donde las conversiones de reactivos se maximizan y se suprimen las reacciones secundarias formadoras de coque. El análisis cinético reveló que una composición de alimentación ideal (fracciones molares de: CH_4= 0,545, CO_2= 0,182, H_2O =0,091) logra una conversión de metano del 33,0% y produce syngas con una relación molar H_2/CO de 3,0 a 800 K, representando el mejor equilibrio entre conversión y selectividad. Finalmente se evaluaron los perfiles térmicos y de composición a lo largo del reactor evidenciando la formación de syngas y el consumo acelerado de metano en el proceso de Tri-reformado. Este trabajo proporciona una metodología computacional robusta para optimizar las condiciones de alimentación del TRM y producir gas de síntesis con composiciones ajustables, ofreciendo perspectivas valiosas para el diseño conceptual y el escalado de reactores para una producción química sostenible.

Palabras clave: *DWSIM*, equilibrio químico, reactor catalítico, simulación computacional, tri-reformado de metano, simulación de procesos, cinética de reacción, gas de síntesis, análisis termodinámico.

1. Introduction

The increasing atmospheric concentrations of greenhouse gases (GHGs), particularly methane (CH_4) and carbon dioxide (CO_2), are major drivers of global climate change, prompting an urgent demand for innovative carbon capture and utilization (CCU) strategies [1]. Sources such as biogas from anaerobic digestion, landfill gas, and industrial flue gases represent significant, underutilized streams of these GHGs. Transforming these waste products into valuable chemical intermediates is a cornerstone of developing a circular carbon economy. A key strategy in this domain is the conversion of CH_4 and CO_2 into synthesis gas (syngas), a versatile mixture of hydrogen (H_2) and carbon monoxide (CO) that serves as a fundamental building block for producing liquid fuels via Fischer-Tropsch synthesis and essential chemicals such as methanol and acetic acid [4]. Several catalytic reforming technologies exist for syngas production. Steam Methane Reforming (SMR) is the most mature industrial process; however is highly energy-intensive and typically produces syngas with a high H_2/CO ratio, which is unsuitable for many downstream syntheses without adjustment [5]. Dry Reforming of Methane (DRM) utilizes CO_2 as an oxidant, directly addressing GHG mitigation, but suffers from severe catalyst deactivation due to carbon deposition (coking). Partial Oxidation of Methane (POM) is an exothermic process that can be more energy-efficient, but it is often difficult to control, carrying risks of thermal runaway and hot spot formation within the reactor [5].

Tri-reforming of methane (TRM), first proposed by Song and Pan, has emerged as a sophisticated and synergistic integration of SMR, DRM, and POM within a single reactor [4]. This process is not merely a combination of reactions but an intelligently designed system that leverages the distinct characteristics of each process to overcome their individual limitations. The exothermic heat generated by POM can be used in-situ to drive the highly endothermic SMR and DRM reactions, significantly improving the overall thermal efficiency of the process and potentially achieving autothermal operation [11]. Furthermore, the presence of steam (H_2O) and oxygen (O_2) as co-reactants actively gasifies carbon deposits, mitigating the severe coking issues that plague DRM and enhancing catalyst stability and longevity [5].

Residual gases such as biogas from anaerobic digestion, landfill gas, and industrial flue gases represent significant and underused sources of these GHGs. These gases typically contain between 50-70 vol% CH_4, 30-50 vol% CO_2, and up to 10 vol% H_2O under saturation conditions [8,19]. This variable composition presents challenges for efficient conversion, requiring precise adjustments in reactant ratios to optimize the tri-reforming process. Biogas enriched with oxidants (water vapor and oxygen) can be transformed into syngas with an adjustable H_2/CO ratio (1,5-2,5), making it highly adaptable for various industrial applications.

Despite its promise, the industrial deployment of TRM is hindered by the complexity of optimizing multiple interacting parameters, including feed composition, temperature, pressure, and catalyst selection [8]. Rigorous process modeling and simulation have become indispensable for navigating this complexity, enabling the systematic exploration of the operational space to identify optimal conditions prior to costly and time-consuming experimental work.

Recent advances in this field include comprehensive thermodynamic analyses of greenhouse gas reforming processes [14,19], the

development of advanced catalysts for tri-reforming applications [20], and integrated techno-economic and environmental assessments of biogas conversion processes [21]. These studies highlight the growing interest in sustainable syngas production routes that simultaneously address greenhouse gas mitigation and resource valorization.

This article is structured as follows: Section 2 describes the materials and methods used in the simulation, including the simulation environment, thermodynamic package, reaction network, and reactor models employed in *DWSIM*. Section 3 presents the results and discussion, first analyzing the thermodynamic behavior of the system and then evaluating the kinetic performance. Finally, Section 4 provides the conclusions and outlines future perspectives.

2. Materials and methods

2.1. Simulation Environment and Thermodynamic Foundation

All process simulations were conducted using DWSIM (version 8.1.2), an open-source, CAPE-OPEN compliant chemical process simulator [13]. The selection of an appropriate thermodynamic property package is critical for accurately predicting the phase behavior and physical properties of the reacting mixture. For this study, the Chao-Seader model was selected. This semi-empirical, activity-coefficient-based model is particularly well-suited for systems containing light hydrocarbons and hydrogen at elevated temperatures, making it a robust and reliable option for simulating syngas production processes [8].

2.2. Governing Reaction Network

The tri-reforming of methane (TRM) process involves a complex network of simultaneous and interrelated reactions. A comprehensive model must account not only for the primary reforming reactions but also for crucial side reactions that significantly influence product distribution, energy balance, and catalyst stability. The model developed in this study incorporates nine fundamental reactions, identified as central to the TRM mechanism, as detailed in Table 1.

Table 1. Governing reactions in the methane tri-reforming process

ID	Reaction Name	Reaction	ΔH (kJ/mol)
R1	Dry Reforming (DRM)	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	+247,0
R2	Steam Reforming (SMR)	$CH_4 + H_2O \rightarrow CO + 3H_2$	+206,0
R3	Partial Oxidation (POM)	$2CH_4 + O_2 \rightarrow 2CO + 4H_2$	-36,0
R4	Total Oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-880,0
R5	Water-Gas Shift (WGS)	$CO + H_2O \rightarrow CO_2 + H_2$	-41,0
R6	Methane Decomposition	$CH_4 \rightarrow C + 2H_2$	+75,0
R7	Boudouard Reaction	$2CO \rightarrow C + CO_2$	-172,0
R8	Coke Gasification (H_2O)	$C + H_2O \rightarrow CO + H_2$	+131,0
R9	Coke Oxidation (O_2)	$C + O_2 \rightarrow CO_2$	-394,0

2.3. Reactor Models and Simulation Setup

Two distinct reactor models were implemented in *DWSIM* to analyze the TRM process from both a thermodynamic and a kinetic perspective.

2.3.1. Equilibrium Analysis (RGibbs Reactor)

To determine the maximum achievable conversions and product yields as dictated by thermodynamics, an equilibrium reactor model (RGibbs) was used. This model calculates the chemical and phase equilibrium of the reacting system by minimizing the total Gibbs free energy, independent of reaction kinetics or catalyst properties. This analysis provides a crucial benchmark, defining the theoretical performance limits of the process under specified conditions of temperature, pressure, and feed composition. The simulations were conducted across a temperature range of 400 K to 1100 K at a constant pressure of 1 atm [12].

2.3.2. Kinetic Analysis (PFR Reactor)

To simulate the performance of a practical industrial reactor, a one-dimensional, pseudo-homogeneous Plug Flow Reactor (PFR) model was employed. This model accounts for reaction kinetics and residence time. The simulated reactor has an internal diameter of 5 cm and a length of 1,5 m, with a total molar flow rate of 100 mol/h (equivalent to a GHSV of 12.000 h^{-1}). The catalyst used was Ni/ZrO_2 (5 wt% Ni) with an apparent density of 1,2 g/cm^3 and a bed porosity of 0,4 [3,13].

Although nine fundamental reactions were considered in the thermodynamic analysis, the kinetic model is limited to the three main reactions (R1, R2 and R5), because these represent more than 95% of the global process kinetics according to previous studies [3, 16, 20]. The oxidation reactions (R3, R4) and coke formation reactions (R6, R7, R8, R9) are considered implicit in the model through the kinetic parameters of the Ni/ZrO_2 catalyst and its behavior under the studied operating conditions [3, 20]. This simplification is justified because detailed experimental studies have demonstrated that the net effect of these secondary reactions is incorporated in the effective kinetic parameters determined for the main reactions [20].

The PFR simulations were conducted under non-isothermal non-adiabatic conditions, considering the coupling between material and energy balances to capture the thermal effects of exothermic and endothermic reactions. This allows for more accurate modeling of the real thermal behavior of the reactor [12, 20].

An important consideration is that the differences in feed compositions between the equilibrium and kinetic models arise because the Gibbs model (equilibrium) includes solid carbon to evaluate the tendency toward coke formation, while the kinetic model uses a feed more representative of real operating conditions with biogas enriched with oxidants. This approach allows for evaluating both the thermodynamic limit and the practical performance of the process [14, 20].

The loads represent different operating strategies: Load 1 (balanced), Load 2 (methane-rich), and Load 3 (oxidant-rich). The selection of Load 1 as optimal is based on optimality criteria that consider not only individual conversions but also the efficient utilization of all reactants, catalyst stability, and feasibility for large-scale industrial application as showed in Table 2.

Table 2. Molar feed compositions for simulation scenarios.

Component	***L1***	***L2***	***L3***
Equilibrium Model Feed (Molar Fraction)			
CH_4	0,286	0,370	0,196
CO_2	0,114	0,111	0,118
H_2O	0,114	0,111	0,118
O_2	0,200	0,222	0,176
$C_{(s)}$	0,171	0,111	0,235
Kinetic (PFR) Model Feed (Molar Fraction)			
CH_4	0,545	0,706	0,375
CO_2	0,182	0,118	0,250
H_2O	0,182	0,118	0,250
O_2	0,91	0,59	0,125
Kinetic parameters			
Reaction	E_{act} KJ/ mol		K_0 mol $g_{cat}h^{-1}$
Steam reforming	117		8,41E4
Dry Reforming	87,1		1,07E3
Water Gas Shift	67,33		4,24E2

Li=reactor Load. Where i=1,2,3.

The inclusion of solid carbon in the equilibrium feed represents a specific condition adopted from the reference study, designed to evaluate the system's thermodynamic tendency toward coke formation and gasification.

3. Results and Discussion

3.1. Thermodynamic analysis

The simulation results are presented in two parts. First, the thermodynamic analysis establishes the feasibility and theoretical limits of the TRM process. Second, the kinetic analysis evaluates the performance within a PFR (Figure 1), providing insights into practical reactor operation and the selection of an optimal feed composition.

The Figure 1 shows the PFR reactor in DWSIM:

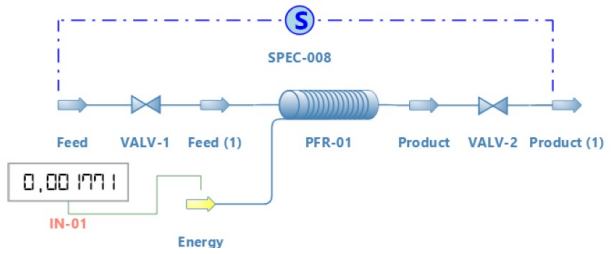


Figure 1. Model PFR reactor simulated in DWSIM.

Figure 2 ilustrates the variation of the natural logarithm of the equilibrium constant for the nine governing reactions as a function of inverse temperature.

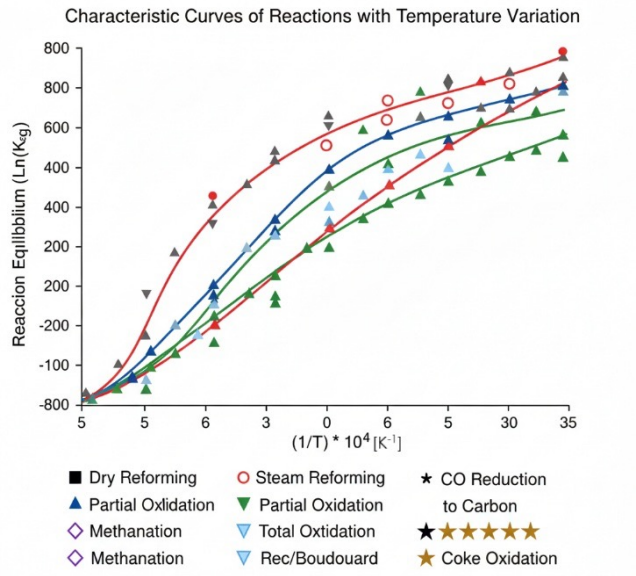


Figure 2. Characteristic curves of the equilibrium constants (Ln(Keq)) for the nine governing reactions of the TRM process as a function of inverse temperature. The plot demonstrates that high temperatures favor the desired reforming reactions (R1, R2) while suppressing the main coking reaction (R7).

This analysis confirms that the primary endothermic reforming reactions—DRM (R1) and SMR (R2)—are strongly favored at higher temperatures (lower 1/T), as indicated by their large, positive lnK values above approximately 700 K.

Conversely, the primary coke-forming pathway, the Boudouard reaction (R7), becomes thermodynamically unfavorable at these temperatures, with its equilibrium shifting strongly towards the reactants (CO). This provides a clear thermodynamic basis for operating the TRM process at high temperatures to maximize syngas yield while simultaneously suppressing catalyst deactivation by coking. The exothermic POM reaction (R3) remains favorable across the entire temperature range. The equilibrium conversions of the primary reactants, CH_4 and O_2, for the three feed loads are compared in Figure 3.

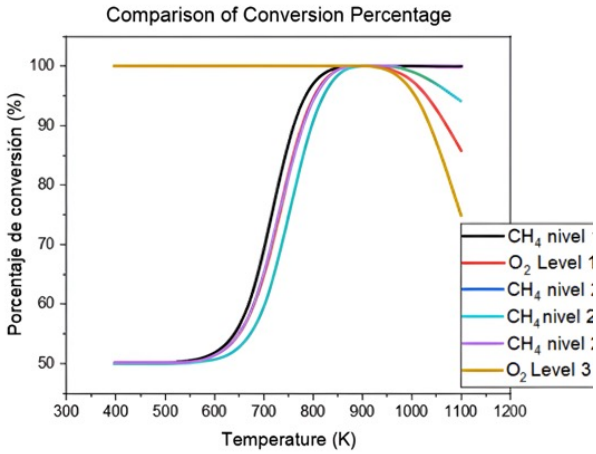


Figure 3. Comparison of equilibrium conversion for methane (CH_4) and oxygen (O_2) as a function of temperature for the three investigated feed loads. The results highlight the optimal operating window above 800 K where methane conversion is maximized.

For all loads, oxygen conversion remains nearly complete across the entire temperature range, due to the high exothermicity of the oxidation reactions. Methane conversion, by contrast, shows a strong temperature dependence, beginning at approximately 50% at 600 K and increasing sharply to near-complete levels conversion (>95%) above 800 K. This transition marks the onset of dominance by the endothermic reforming reactions.

The analysis of the system's Gibbs free energy change (ΔG) further refines the thermodynamic operating window of the process. As demonstrated in the reference study [14], the reactions remain highly spontaneous ($\Delta G << 0$) at moderate temperatures (500-800 K) but gradually approaches equilibrium ($\Delta G \rightarrow 0$) at temperatures above 800 K. This behavior indicates that further temperature increases beyond approximately ~900 K yields diminishing returns in terms of conversion, establishing an optimal thermodynamic operating range between 800-900 K.

3.2. Kinetic Performance and Reactor Profile Analysis

While thermodynamic analysis establishes the potential of the process, kinetic analysis — performed using the PFR model— provides insight into its practical performance within a finite-volume reactor. Table 3 summarizes the key performance indicators for the three feed loads, simulated at an isothermal temperature of 800 K and 1 atm pressure.

Table 3. Comparative PFR Reactor Performance at 800 K, 1 atm.

Parameter	***Load 1***	***Load 2***	***Load 3***
CH_4 Conversion (%)	32,98	11,24	52,67
CO_2 Conversion (%)	26,37	13,39	28,36
H_2/CO Molar Ratio	3,00	3,00	3,00
H_2 Yield (mol/s)	0,3966	0,2054	0,4246
Residence Time (s)	15,21	10,14	12,78

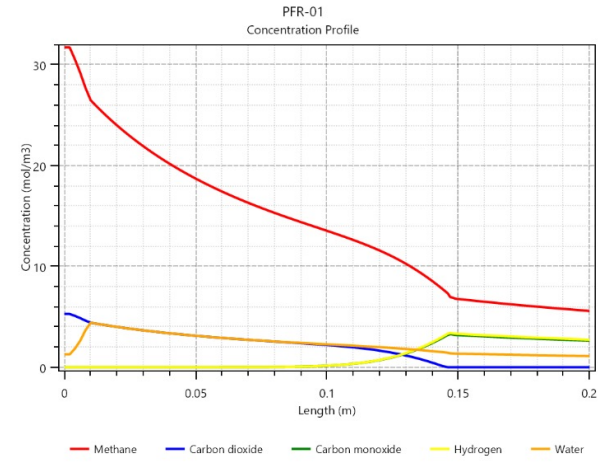
Note: Performance metrics calculated from PFR simulations based on data from [14]. CO_2 conversion and H_2 yield are calculated based on outlet molar flows relative to inlet flows.

The kinetic results reveal significant performance differences between the feed compositions. Load 3 achieves the highest methane conversion (52,67%), but this result must be interpreted with caution. Load 3 contains the lowest relative amount of methane and the highest the highest proportion of oxidants (CO_2 and O_2) (see Table II). The elevated conversion is likely driven by the fast, exothermic oxidation reactions rather than the desired, slower endothermic reforming reactions. This behavior may result in reduced selectivity towards syngas and potential thermal management issues in industrial applications.

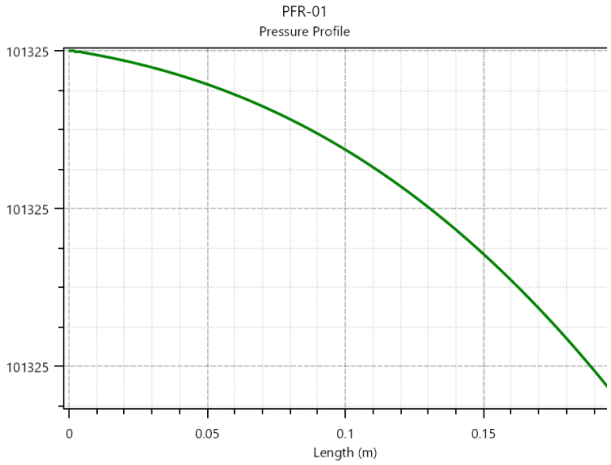
Load 2, which is methane-rich, shows the lowest conversion for all reactants, indicating that the oxidants are the limiting species.

This study identifies Load 1 as "ideal" because it provides the most equitable and efficient use of all reactants to produce syngas, avoiding a regime dominated by simple oxidation. It represents a true "tri-reforming" mode of operation, where all three primary reactions contribute significantly. Although its methane conversion (32,98%) is lower than that of Load 3, it achieves a substantial conversion of CO_2 (26,37%) while maintaining high hydrogen production. The consistent H_2/CO ratio of 3.0 across all loads in the PFR simulation is primarily an artifact of the kinetic model focusing on the main reactions and suggests a strong influence from the SMR reaction stoichiometry under these conditions.

The optimality criteria used to select Load 1 as ideal were: Maximum net syngas production per unit of reactant consumed, a favorable energy balance that allows autothermal operation, significant conversion of both CH_4 and CO_2 (not just one of them), low thermodynamic tendency for coke formation and practical feasibility for large-scale industrial implementation.



(a)



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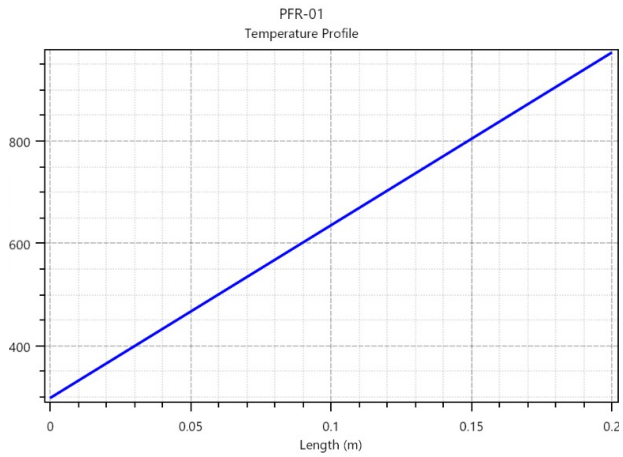

(c)

Figure 4. Concentration profiles (a), pressure (b), and temperature (c) along the normalized length of the PFR for the ideal feed composition (Load 1) under non-isothermal conditions at 1 atm.

Analysis of the concentration profiles (Figure 4a) reveals that the optimal reactor length would be approximately 0,25 m (16,7% of the total simulated length), the point at which 95% of the maximum syngas production is achieved. Increasing the length beyond this point would result in marginal conversion gains (less than 3%) with a significant penalty in capital costs.

The temperature profile (Figure 4c) reveals an initial rise from 800 K to 875 K within the first 10 cm of the reactor, attributed to the exothermic partial oxidation reaction (R3), followed by a gradual decrease to 825 K at the reactor outlet due to the endothermic reforming reactions (R1, R2). This behavior confirms the inherent thermal coupling of the tri-reforming process, where heat generated by exothermic reactions is used in situ to drive endothermic reactions, improving the overall energy efficiency of the process. The reactor inlet and outlet temperatures were 800 K and 825 K respectively, selected to maintain the reactor within the optimal operating window (800-900 K) identified in the thermodynamic analysis.

4. Conclusions

The tri-reforming of methane (TRM) process is thermodynamically favorable at elevated temperatures, with an optimal operating window identified between 800 K and 900 K at atmospheric pressure. Within this range, high conversions of methane and carbon dioxide are achieved, and the equilibrium strongly disfavors solid-carbon formation, thereby mitigating one of the main causes of catalyst deactivation.

The kinetic analysis demonstrated that feed composition is a critical determinant of reactor performance. A balanced feed (Load 1, with molar fractions of: CH_4= 0,545, CO_2= 0.,82, H_2O= 0,091, O_2=0,091) was identified as the ideal case. It provides a robust compromise between high reactant conversion and efficient syngas production, operating in a true tri-reforming regime where steam reforming, dry reforming, and partial oxidation all contribute significantly.

The PFR model revealed distinct reaction zones, with rapid partial oxidation occurring at the reactor inlet, followed by slower, sustained endothermic reforming. This insight is crucial for reactor design, thermal management, and catalyst selection.

The simulation results provide a strong quantitative basis for the conceptual design of a lab-scale TRM reactor. The identified optimal conditions and feed ratios serve as a valuable starting point for future experimental investigations focused on catalyst development, long-term stability testing, and process scale-up, which are essential steps toward the industrial application of this promising GHG valorization technology.

The results obtained are consistent with recent experimental studies. Zhang et al. [13] reported methane conversions of 35-40% at 800 °C with a similar Ni/ZrO_2 catalyst in a fixed-bed reactor, values close to those calculated for Load 1 in this study. Similarly, the observed temperature profiles coincide with those reported by Díez-Ramírez et al. [12] in their TRM simulation studies.

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