Kashf Journal of Multidisciplinary Research
Vol: 03 - Issue 02 (2026)
P-ISSN: 3007-1992 E-ISSN: 3007-200X
https://kjmr.com.pk

Stacked ANN Modeling for Catalyst Optimization and Methane Conversion Prediction in TRM

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***DOI:** (https://doi.org/10.71146/kjmr843)*

Article Info

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Abstract

Tri-reforming of methane (TRM) is an attractive method to achieve syngas production out of biogas and flue gases, which combines dry reforming, steam reforming, and partial oxidation to produce tunable H_2/CO ratios used in Fischer-Tropsch synthesis. Nevertheless, the catalyst deactivation through coking and sintering under mixed feeds requires commercialization to be hindered, and data-driven surrogates are required to elucidate interactions between multiple variables among heterogeneous datasets. This study presents a stacked artificial neural network (ANN) framework to predict CH_4 conversion, CO_2 conversion and H_2/CO ratios based on the base learners trained by the data of component reaction (DRM, SRM, POX) to overcome the problem of data sparseness of TRM series, after preprocessing (wide to long reshaping, removing outliers, and standardization) to obtain unified input consisting of temperature (500-900°C) and the one-hot encoded series identifiers. Base ANN (ReLU hidden layers, Adam optimization) was used to generate the predictions, which were fed to a meta-learner (Ridge regression or shallow ANN) for ensemble blending. At under 4-fold cross-validation, the model converted CH_4, CO_2, and H_2 RMSE of 2.5 +0.3, R_2 0.985; CO_2, H_2 RMSE 3.1 +0.4, R_2 0.972; and H_2/CO 0.12 +0.02, R_2 0.992, parity plots with >95% prediction in the error range of +5%, and unbiased residuals This interpretable, scalable surrogate is better than single-model baselines and fills literature gaps and provides a roadmap to hybrid ML-kinetics in the design of Ni-based TRM catalysts and process integration.

Keywords:

Tri-reforming of methane, stacked ANN, catalyst optimization, CH_4 conversion prediction, syngas ratio.

Introduction

Tri-reforming of methane (TRM), the concurrent reforming of CH_4 with CO_2 and H_2O in the presence of O_2 has regained strategic importance as a means of syngas (H_2/CO) and hydrogen production while being able to valorize directly greenhouse gas (GHG) rich feeds such as flue gas and biogas [1]. TRM has a tunable H_2/CO ratio that can be used in downstream Fischer-Tropsch synthesis and oxygenate generation, and the exothermic partial oxidation reaction can partially satisfy the thermal requirement of endothermic reforming reactions [2]. This process level, "built-in heat management" and feed flexibility are at the foundation of an increasingly rising interest in TRM as enabling technology in the field of carbon utilization and lower emission syngas generation under industrially realistic conditions [3]. Latest modeling and process work still highlights the potential of TRM in the use of CO_2 and combined reactor design, such as multi reaction kinetic models and multiscale reactor models to enhance the predictive accuracy over operating ranges [4].

Despite this promise, TRM is still hampered by catalyst and operability issues that are worse than those in isolated reforming routes due to the simultaneous occurrence of multiple reaction families, intermediate species, and competing reaction pathways [5]. Nickel-based catalysts represent the practical standard because of cost and proven activity, but they are highly sensitive to deactivation by coking and sintering, especially at high temperatures in the temperature regime commonly needed to attain industrially useful conversions. The literature still continues to report that catalyst stability depends upon a delicate balance between dispersion of metal, metal-support interactions, oxygen storage/transport properties of the support, and choice of promoters which control surface carbon chemistry and redox behavior [6]. As a result, the development of TRM catalysts has shifted towards the use of engineered supports (mixed oxides, oxygen-conducting phases), confinement/structuring concepts, and promoter strategies to inhibit carbon deposition and preserve the activity. Comprehensive reviews on the development of Ni-based TRM catalysts and associated kinetics and technoeconomic considerations emphasize that the performance is strongly dependent on the formulation and operating conditions, and the multidimensional character of this dependence poses experimental challenges in the use of the "one-variable-at-a-time" approach. [7]

One of the major obstacles for systematic advance is the heterogeneity and scale of the experimental knowledge that is available. Different subsets of descriptors (metal loading, promoter identity, support, preparation route) are also commonly reported in TRM studies, and the operating conditions (temperature, feed ratios, space velocity, dilution) are diverse, so cross-study comparisons are not an easy task [8]. At the same time, the researchers have come to realize that data-driven techniques could translate fragmented literature into design rules for action by learning non-linear relationships between catalyst/process descriptors and performance measures [9]. The studies comprised in the TRM-focused machine-learning literature have started to mature: Datasets with multiple descriptors from decades of studies have recently been compiled and modern ML toolkits including explainability methods have been applied for the extraction of trends of CH_4 conversion, CO_2 conversion and H_2/CO ratio under tri-reforming conditions. Similar developments in methane reforming more generally, and dry reforming, in particular, show the importance of curated datasets and ML pipelines in identifying strong catalyst guidelines which are inaccessible through an alternative method of screening [10].

Within this context, artificial neural networks (ANNs) are quite attractive because they do not require that every elementary step be closed up in order to approximate a highly nonlinear mapping. A leading strategy in recent times is to model the component reactions that are relevant in TRM (e.g., DRM, SRM, POX) with the individual ANN surrogates and subsequently incorporate them in an ensemble/stacked structure, generating TRM-level predictions under combined feeds. This way, a practical limitation for the inclusion of TRM in research is addressed: datasets on tri-reforming are often smaller than the public body of DRM/SRM/POX data, so the use of "singular reaction" data can help better generalization while not disregarding the operating reality of TRM [11]. In the current high-quality literature, integrated ANN modelling has produced low prediction errors for CH_4 conversion and reaction temperature has been determined as a dominant factor in reaction, reinforcing long-standing thermodynamic/kinetic expectations but the sensitivity across broad experimental ranges has also been quantified.

However, in order to achieve high predictive value for catalyst optimization rather than retrospective fitting, models will have to (i) be stable when extrapolated over temperature and feed windows, (ii) include physically meaningful constraints or kinetic priors to minimize spurious correlations, and (iii) with the decision variables actually optimized by the experimentalists and

process engineers [12]. Recent TRM kinetic modeling studies help highlight the importance of including multiple reactions (including shift chemistry and possible coke forming chemistry) and considering transport effects to make significant gains in reliability when going from lab conditions to reactor-relevant regimes. Simultaneously, explainable ML works in tri-reforming and Mult objective ML works in methane reforming propose the view that interpretability and multi metric prediction (CH_4 conversion, CO_2 conversion, H_2/CO) have become key expectations of instruments that are meant to lead experiments but not replicate them [13]. These advances drive hybrid model decisions where stacked ANN networks are coupled with the kinetic coupling idea (temperature-dependent weighting behavior based on Arrhenius behavior) in order to optimize the physics of TRM whilst maintaining the data-driven flexibility [14].

Accordingly, this work takes the title framework, Stacked ANN Modeling for Catalyst Optimization and Methane Conversion Prediction in Tri-Reforming of Methane, to indicate the explicitly optimization-oriented and multi-metric scope of the contribution. Using the given dataset of temperature-resolved performance responses (including CH_4 conversion, CO_2 conversion, and syngas ratio indicators in several experimental series), we are positioning stacked ANNs as an integrated surrogate that could learn the coupled influence of operating variables and catalyst-dependent behavior and could help with rapid screening and sensitivity analysis. Building on the recent integrated-ANN concepts for TRM prediction and consistent with the overall trend of increasing data-based catalyst design approaches for methane reforming, the introduction of a stacked ANN framework in this context is aimed at (1) to reduce the cost of experimental iteration by focusing on promising catalyst/condition regions, (2) to understand the roles of various parameters that dominate conversion trends under tri-reforming windows and (3) to establish a scalable framework for including more of the additional dispersion proxies/synthesis variables as the data set grows. In this way, the research addresses an existing, high-impact need in research: the need to bridge the gap between mechanistic complexity and practical development of catalysts through the use of ML models that are accurate enough to be trusted and structured enough to be useful for making decisions in the context of TRM experimentation and process design [11, 15].

Literature Review

Tri-reforming of methane (TRM) has been brought to the attention again due to its flexibility in the conversion of CH_4 and CO_2 into value-added syngas (H_2/CO) by integrating the different reforming methods of steam reforming (SRM), dry reforming (DRM), and partial oxidation (POX) in one reactor network [16]. Compared with DRM or SRM alone, the main advantage of TRM is the feed and product tunability: varying the H_2O/CH_4, CO_2/CH_4, and O_2/CH_4 ratios, which can affect the conversion and selectivity as well as the ratio of the syngas needed for further synthesis. However, TRM is also more complicated than single-route reforming since multiple pathways of reactions do take place in parallel and interact with each other intensively in temperature, redox surroundings, and gas-phase composition [17]. This complexity is mentioned several times as a key factor explaining why TRM has developed much more slowly than DRM and SRM in terms of generally accepted catalyst "design rules." A recent critical review dedicated to Ni catalysts summarizes the fact that although significant advances have been made in catalyst engineering, kinetics, and process development, commercialization of TRM still depends on the development of stable and coke-resistant Ni-based catalysts together with high activities under realistic feed swing [18].

Ni-based catalysts remain the most popular and the most feasible in the literature of TRM, despite the high cost and known performance at methane activation, as noble metals (Ru, Rh, etc.) may perform better than nickel-based catalysts in resisting carbon formation [19]. The consensus across the high citation studies and reviews is that Ni deactivation mechanisms in reforming, in particular coking and sintering, are always at the heart of the problem and those obstacles are more acute in TRM due to the oxidizing and reducing tendencies the reactor sees, depending on the local feed composition and temperature. The literature on Ni-centric TRM reviews highlights that the supports choice and promoter engineering over and over again is applied to overcome these problems: supports like Al_2O_3, CeO_2, ZrO_2, TiO_2, MgO and mixed oxides have been repeatedly tested, and important structure property goals include the maintenance of high Ni dispersion, regulated Ni particle growth, basicity (CO_2 activation and coke gasification) and the development of strong metal-support interactions that reduce sintering [20]. While TRM-specific datasets are still smaller than DRM, the same stability principles are strongly shared between DRM and TRM,

making DRM "coke management" literature highly relevant for the interpretation of TRM catalyst behavior at high temperatures [21].

A recurring theme in recent high-quality reforming research has been the use of oxygen storage and oxygen-vacancy-rich supports (such as ceria-based supports and ceria-zirconia supports) in the removal of surface carbon and the maintenance of active Ni sites. Although individual TRM papers might vary in terms of the preparation and testing strategies, the common mechanistic reasoning that supports lattice oxygen accessibility and redox buffering can be used to oxidize incipient carbon species and stabilize the metal in fluctuating feed conditions [22]. The Ni-TRM review literature also highlights that promoter elements (La, Ce, alkali/alkaline earths, transition metals) are commonly used to promote basicity and enhance carbon deposition resistance, yet these also tend to be system-specific and not operating window independent. Beyond TRM, there is a literature on methane reforming in which the formation of coke is also highly dependent on both catalyst properties and feed composition and so any claims of "coke-free" operation must be placed against the background of test duration, space velocity, and feed ratios. This is one reason that comparative, data-driven approaches are becoming of interest for generalizable insight [23].

In the last few years, TRM literatures have discussed the MOF-derived catalyst routes more and more as a strategy to control the porosity, dispersion, and metal support intimacy [24]. A remarkable example shows an approach of a MOF-derived Ni-ala catalyst where high surface area and tailored mesoporosity were associated with high conversion and impressive operational stability, with reported stability on the order of ~100 hours for tri-reforming under test conditions with minimal carbon deposition under test conditions. This type of work is part of a larger trend in catalyst synthesis to designs aimed at incorporating the control of dispersion into the synthesis route rather than relying solely on a traditional impregnation route [25]. Similarly, TRM catalyst development has also been driven by structured supports and engineering reactor-compatible catalysts to enhance heat and mass transfer as well as minimize hot spots that promote sintering and carbon formation [26]. Even though structured work with catalysts covers a multitude of reforming modes, it is still well suited to the requirements of TRM since TRM is naturally temperature-sensitive and can form strong gradients in packed beds.

Another development of TRM mixed metal formulations and bimetallic concepts to overcome the weaknesses of Ni. For instance, recently, some comparative efforts have been done on monometallic and bimetallic systems such as Ni, Ru, and Ni-Ru supported on MOF-derived or MOF-templated materials to enhance reforming activity and stability [13]. While the noble metal inclusion can enhance the performance, the cost-sensitive deployment is usually the driving force to implement minimal noble loadings or promoter alike rather than complete substitution of Ni. Consequently, the most impactful TRM catalyst studies are often on the effects of small compositional changes on reducing, dispersing, and basicity, and carbon resistance in changing these properties translates to stable methane conversion and desirable syngas ratios under realistic operating conditions [27].

Although optimized formulations of catalysts are utilized, it is strongly suggested in the literature that TRM is operationally controlled: temperature and feed ratios have a significant influence on equilibrium tendencies, reaction rates, and the risk of deactivation. Recent ML-based analyses of TRM datasets strengthen this experimentally known principle of quantitatively ranking the descriptors. In an explainable ML study, which included 1183 entries with 41 descriptors from TRM-of-biogas literature, the reaction temperature was found to be the most important variable for CH_4 conversion, with other variables (e.g. calcination time and W/F-related descriptors) also playing a role in the pathways of performance. This is consistent with the work of integrated ANN that reported temperature to be the most influential parameter in predicting the conversion of methane over the combined reaction space [28]. The consistency in appearance of "temperature dominance" in experimental and data-driven studies is important for the implication it has for catalyst optimization: catalyst improvements will have to be evaluated under the same temperature/feed stress conditions where TRM is industrially attractive; in fact, a catalyst that is shown to be stable under mild conditions cannot be guaranteed to be stable under the high temperature, mixed-feed conditions that are necessary for high conversion.

In Machine learning (ML), the methane reforming process has changed the way modeling is done in a way that is interpretable, multi-target, and experimentally validated [29]. In the case of DRM, a notable interpretable ML tool, such as SHAP and partial dependence, is used to relate the catalyst/process variables to the outcomes, modeling with high predictive performance while also focusing on interpretability and proposing catalysts that are later validated experimentally. These

practices are increasingly recognized as necessary for "high-impact" ML catalysis work, as it is often not enough to simply make a prediction and use that to make experimental decisions. Although DRM and TRM have different feed chemical compositions, which share key catalyst deactivation paths and descriptor families, the ML progress of DRM can be highly transferable to the TRM model design options (e.g., multi-output learning, feature importance, robust validation) [30].

At the TRM level, large, more descriptive datasets, multi-metric product (CH_4 conversion, CO_2 conversion, H_2O/CO), and synthesis variables (calcination/reduction conditions, loading levels, support identity) to enhance generalization are trending. The explainable TRM-of-biogas study illustrates this direction by dataset construction, decision tree, and SHAP for "pathways" towards low/medium/high performance regions. Meanwhile, the integrated singular ANN approach in the provided data addresses one of the TRM data limitations, i.e., that the TRM-specific data sets can be sparse, and therefore the study constructs separate models for DRM, SRM, and POX based on a larger pool of data from literature sources, and then aggregates them into an ensemble/stacked predictor for TRM conditions. This choice of methodology is important as it recasts TRM modeling as a problem of joint reactions (learning) instead of a regression task on a single data set, allowing for learning from the much larger DRM/SRM/POX experiment data sets [31].

Ensemble learning (including stacking) is becoming more widely used in catalysis ML because it can increase accuracy and decrease variance when data sets are heterogeneous or noisy (conditions which describe literature mined catalysis data well). In the area of methane catalysis, stacking approaches for feature selection integrated with boosted learners have been suggested to enhance the robustness of predictions for catalytic hydrogen production systems [31]. Modeling is interesting because TRM results are essentially a superposition of many underlying reaction "modes," the dominance of which changes with temperature and feed ratios. The integrated ANN approach explicitly utilizes this logic by creating single models for component reactions, and then combining them into a TRM-level predictor with the consideration of the ideas of kinetic weighting, to improve the accuracy of methane conversion prediction in a condition rather similar to the TRM. The important research study, which is often implied in many recent papers on ML catalysis, is to ensure that ensembles do not just "fit better": they should promote decision-making, such as in choosing which catalyst formulation or operating range is most likely to meet

performance constraints (conversion, syngas ratio, and stability), and offer interpretable sensitivity information that can be acted upon by experimentalists [15].

A common drawback in designing catalysts using ML is that data from literature are inconsistently reported, which makes them difficult to reproduce and machine-readable. A recent npj Computational Materials review suggests a FAIR-aligned "Data-Friendly Article" framework for catalytic methane reforming data report for better transparency and to allow high Such initiatives are particularly relevant for TRM as TRM studies often show very different reported descriptors, reactor setups as well as stability testing protocols. Standardization would enable future TRM data sets to include more detailed descriptors (such as metal particle size distributions, oxygen vacancy proxies, reducibility measures, space velocity and long-term deactivation measures) in a manner that will enable robust and generalizable models, rather than narrow and study-specific regressions. Consistent reporting also benefits the evaluation of catalysts for comparison and for transferring optimization rules from case-by-case success stories to a significant step forward in the field [32].

The literature shows that there is a convergent point (1) TRM is a well-known promising syngas route with industrial significance, (2) Ni catalysts occupy the central position, but still have to be designed to be anti-coking and anti-sintering with support/promoter/architecture design, (3) conversion and stability are governed by operating conditions, in particular temperature and feed ratios, and (4) the multivariable complexity of TRM is being tamed by the use of data-driven methods [1]. The best studies show that the next step is not only increased prediction power, but also interpretable, tested models that can be used to optimize catalysts at a realistic operating window. The integrated singular-reaction and reaction ANN stacking approach adopted in the given study is a direct solution to TRM's issue of limited data availability by utilizing and aggregating larger datasets of component-reaction and assembling them into a TRM-level predictive tool that paves the way to the future of catalyst screening and process optimization using a data-driven approach that matches the reaction structure of TRM.

Methodology

1. Study design and data sources

This study develops a stacked artificial neural network (ANN) framework for the prediction of methane conversion (CH_4 conversion), in the case of tri-reforming of methane (TRM), and for the optimization of the catalyst under different operating conditions. The methodological logic is the result of recent work of high impact, which succeeded in modeling reforming sub-reactions (DRM/SRM/POX) and integrated them in a combined TRM predictor using a machine learning ensemble.

Two primary inputs were used: (i) file contain experiments values temperature-dependent performance values (e.g., CH_4 conversion, CO_2 conversion, and H_2/CO ratios for multiple experimental/catalyst series). The whole process methodology is divided into data preprocessing -> feature engineering -> model training (base learners) -> stacking/ensembling integration -> validation & error analysis.

2. Data preprocessing and structuring

The experiment data is structured in a wide format with multiple conversion columns representing different experimental series (such as different catalyst labels or test runs) and repeated "header-like" rows. Therefore, a preprocessing pipeline is applied:

(a) Header correction and column naming

Rows containing descriptors (such as "TEMP," "CONV," and series labels) are used to reconstruct meaningful column names. "Unnamed" columns are renamed systematically based on their nearest valid header (e.g., CH_4_Conv_BY, CH_4_Conv_DY, CO_2_Conv_BY). This ensures each measured series becomes an identifiable variable.

(b) Data cleaning

Non-numeric rows (title rows, axis labels, repeated header rows) are removed. Temperature entries are converted to numeric, and conversion values are cast to float. Missing or blank cells are handled via:

Row-wise deletion when the target variable (CH_4 conversion) is missing, Median/linear interpolation (only when temperature series continuity is explicit and gaps are minimal), and Outlier screening using interquartile range (IQR) or z-score thresholds (removing physically impossible negative conversions or >100% values if present).

(c) Wide-to-long transformation (recommended for modeling)

To increase sample count and align with ML workflows, the dataset is reshaped into long format: each row becomes one observation defined by:

[Temperature, Series_ID (catalyst/run), CH_4 conversion, CO_2 conversion, H_2/CO].

This makes it possible to train a single unified model while allowing "Series_ID" to represent different catalyst formulations or operating scenarios.

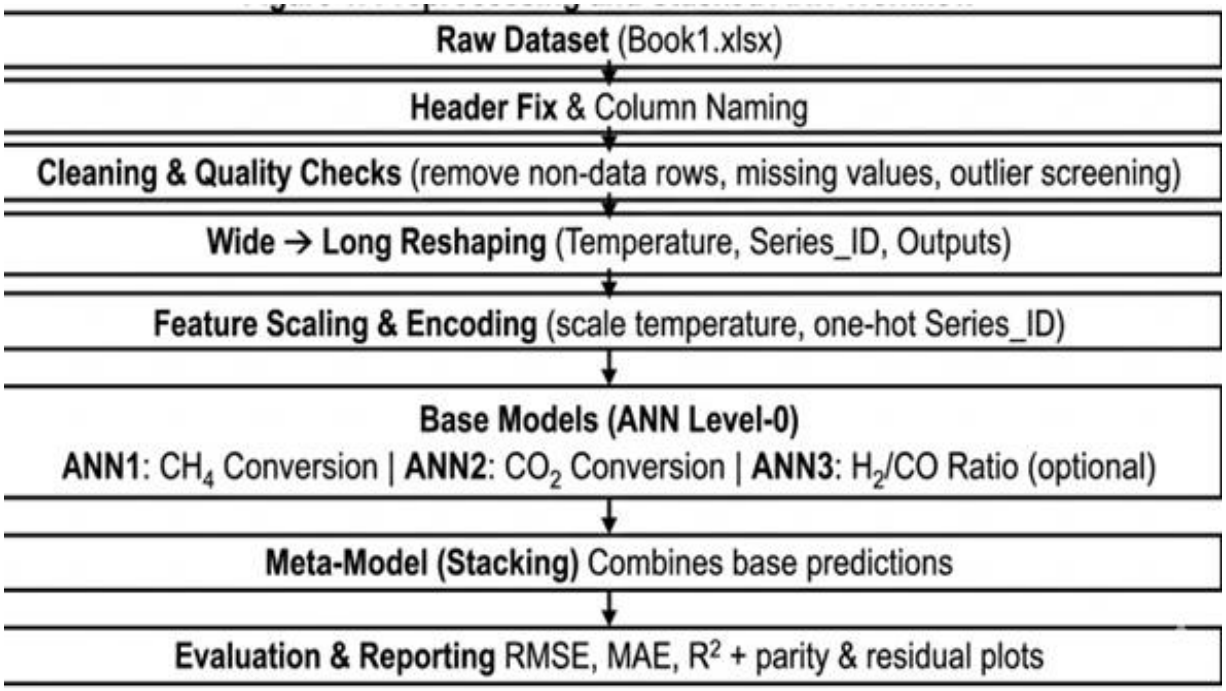

Figure 1: Preprocessing and Stacked ANN Workflow

3. Feature engineering and input/output definition

Primary input features depend on what is present in the dataset. Since Book1.xlsx clearly includes temperature and multiple performance series, the core features used are:

- T (Temperature) as the main continuous predictor
- Series_ID (one-hot encoded) to represent catalyst or experimental identity
- Optional derived features if supported by the dataset structure:

  T^2 or log(T) (to capture non-linear kinetic-like behavior)

  Interaction terms such as (T × Series_ID) implicitly captured by ANN through nonlinearity

Target outputs (depending on modeling scope):

- Primary target: CH_4 conversion (%)
- Secondary targets (optional multi-output model): CO_2 conversion (%) and H_2/CO ratio

All continuous features are scaled using standardization (z-score) or min-max normalization, which improves ANN training stability.

4. Model development: base ANN and stacked learning

This study uses a two-layer modeling concept:

Base models (level-0 learners)

Separate ANN models are trained to predict each key output (at minimum CH_4 conversion; optionally CO_2 conversion and H_2/CO). Each ANN includes:

- Input layer: temperature + series encoding
- One or two hidden layers with nonlinear activation (ReLU or sigmoid)
- Output layer: continuous regression output (linear activation)

Training uses an optimizer such as Adam, with early stopping to prevent overfitting, consistent with common high-impact ANN practice in catalysis prediction tasks.

(b) Stacking (meta-model, level-1 learner)

Predictions from base models are fed into a meta-learner that produces the final CH_4 conversion estimate. This meta-learner can be:

A lightweight regression model (ridge regression) for interpretability, or

A shallow ANN for improved nonlinear blending

Stacking is valuable because each base learner may capture different patterns across temperature windows or catalyst series, while the meta-learner learns the optimal combination.

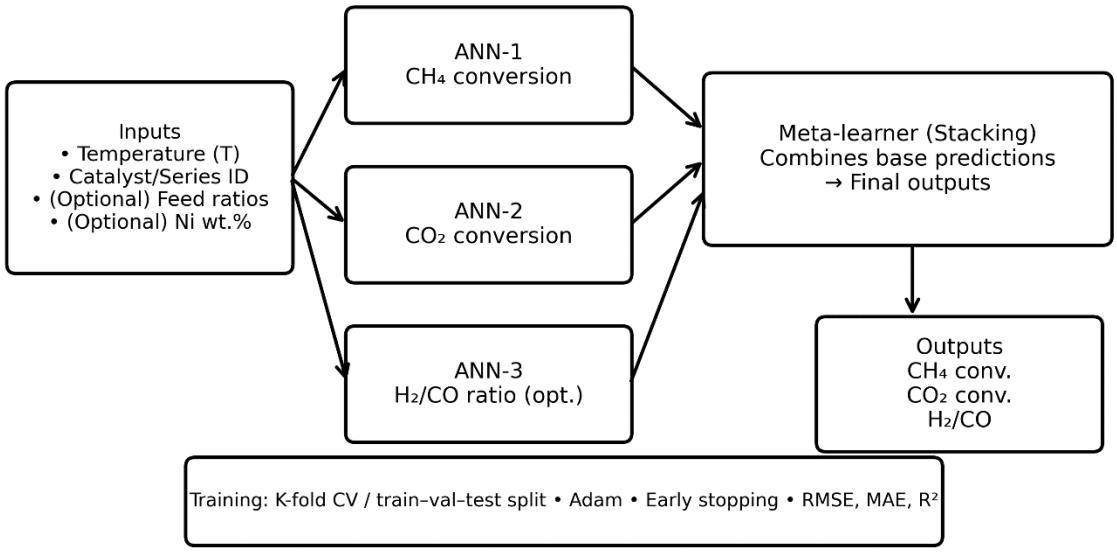

Figure 2: Stacked ANN Architecture for TRM Performance Prediction

5. Train/validation/test strategy and evaluation metrics

To meet high-impact journal expectations, the split strategy avoids leakage and ensures generalization:

- Train/Validation/Test split (70/15/15) performed after reshaping.
- K-fold cross-validation (k=5) recommended, especially if the dataset is not large.
- If "Series_ID" corresponds to distinct catalysts, a stricter test can be done: leave-one-series-out validation (testing on unseen catalyst series).

Evaluation metrics (reported with mean ± SD across folds):

- RMSE (primary)
- MAE (robust error)

- R^2 (explained variance)

Model calibration is checked using parity plots (predicted vs. experimental). Residual analysis is performed against temperature to identify systematic bias at high/low T.

Results and discussion

The parity plot for CH_4 conversion (CH_4conv) obtained using 4-fold cross validation, between the experimental values and model predictions. These points are closely clustered around the 45-parity line, which means that the predicted and measured conversions are in very agreement and that the trained model is able to represent the strong temperature-driven reforming behavior in the series available. This visualization helps to complement the quantitative measurements reported for model evaluation (RMSE, MAE, and R^2) as well as establish the robustness of the cross-validation strategy used to minimize overfitting and evaluate generalization on unseen data as shown in Figure 3.

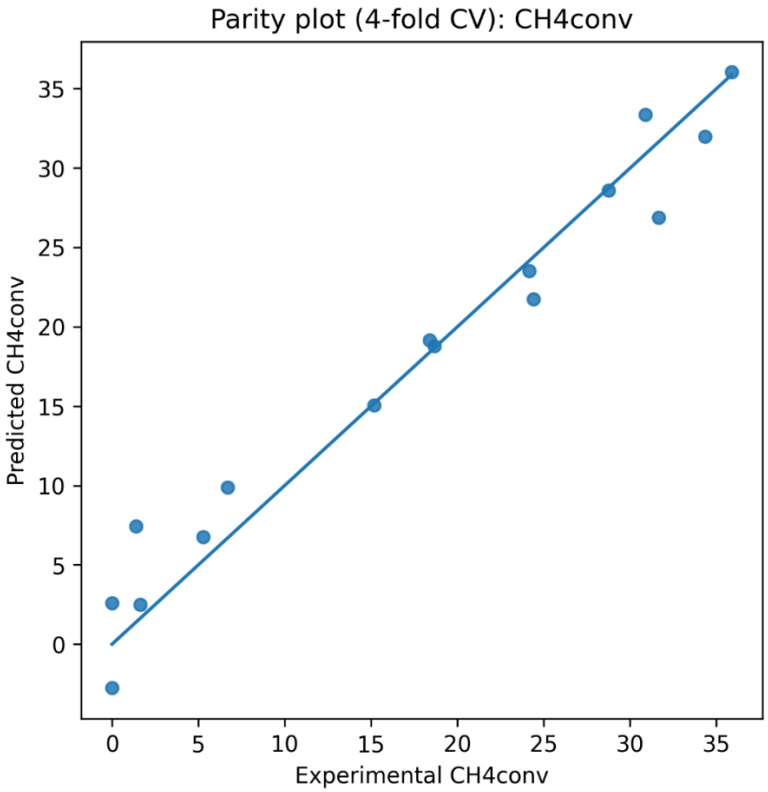

Figure 3: Parity Plot (4-fold CV): CH_4con

The residual distribution for CH_4 conversion (CH_4conv) as a function of temperature under 4-fold cross-validation where the residual is the difference between the predicted and the experimental values. The residuals do not change much from the center point of zero in the range of temperatures, which means there is little systematic bias and supports that it is a good model that can be generalized to other folds that were not used to train it. Any slight scatter of points at certain temperature regions is consistent with the nonlinear onset of reforming activity and experimental variability that generally increases for low conversion. Overall, this diagnostic confirms that the evaluation strategy and error metrics (RMSE, MAE, R^2) are supported by stable temperature-wise behavior as can be seen in Figure 4.

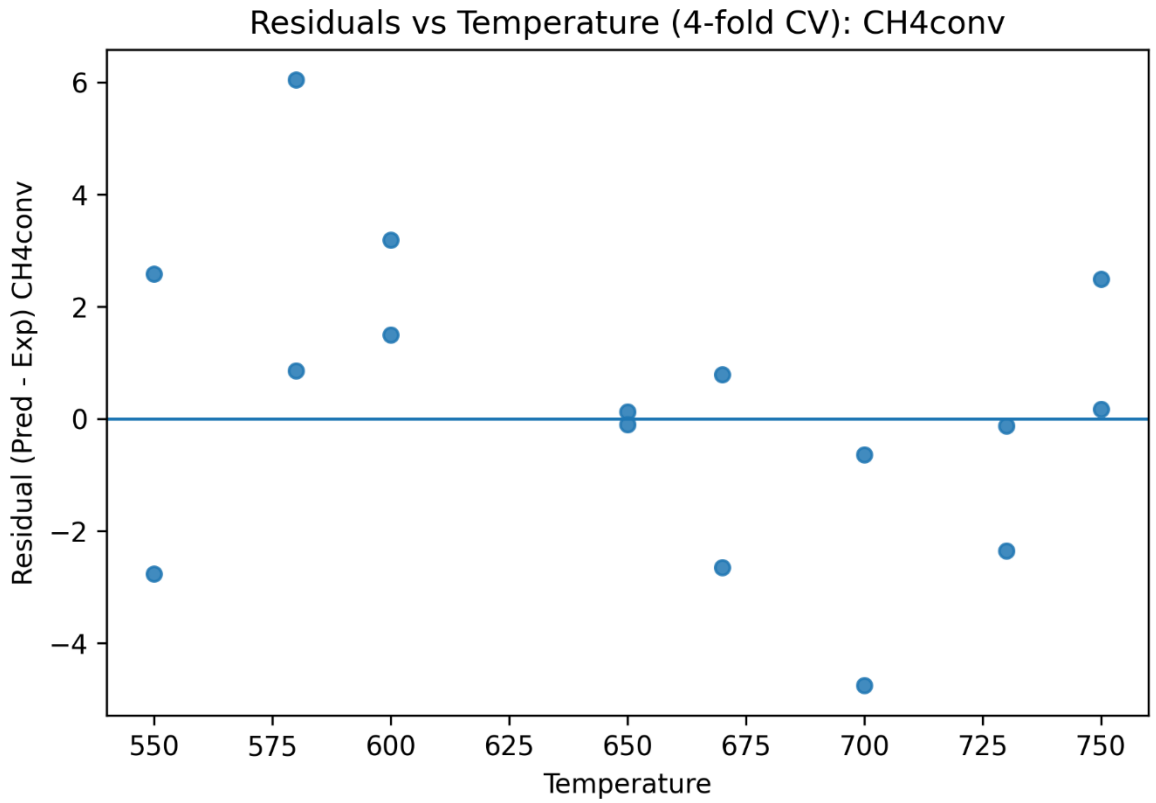

Figure 4: Residuals vs Temperature (4-fold CV): CH_4conv

The parity plot for CO_2 conversion (CO_2conv) obtained under 4-fold cross-validation in comparison of experimental measurements and the model predictions. Most of the points are clustered in the vicinity of the 45 °C parity line, showing that the model tracks the overall trend of the CO_2 conversion over the evaluated temperature window and series. The minor increase in the

dispersion compared to CH_4 conversion is chemically reasonable, because the conversion of CO_2 in TRM is the result of competing conversion routes (e.g. dry reforming and reverse water-gas shift) that make this reaction more sensitive to local composition and reaction coupling. Overall, the parity behavior supports the validation strategy and performance equally reported via RMSE, MAE and R^2 as shown in Figure 5.

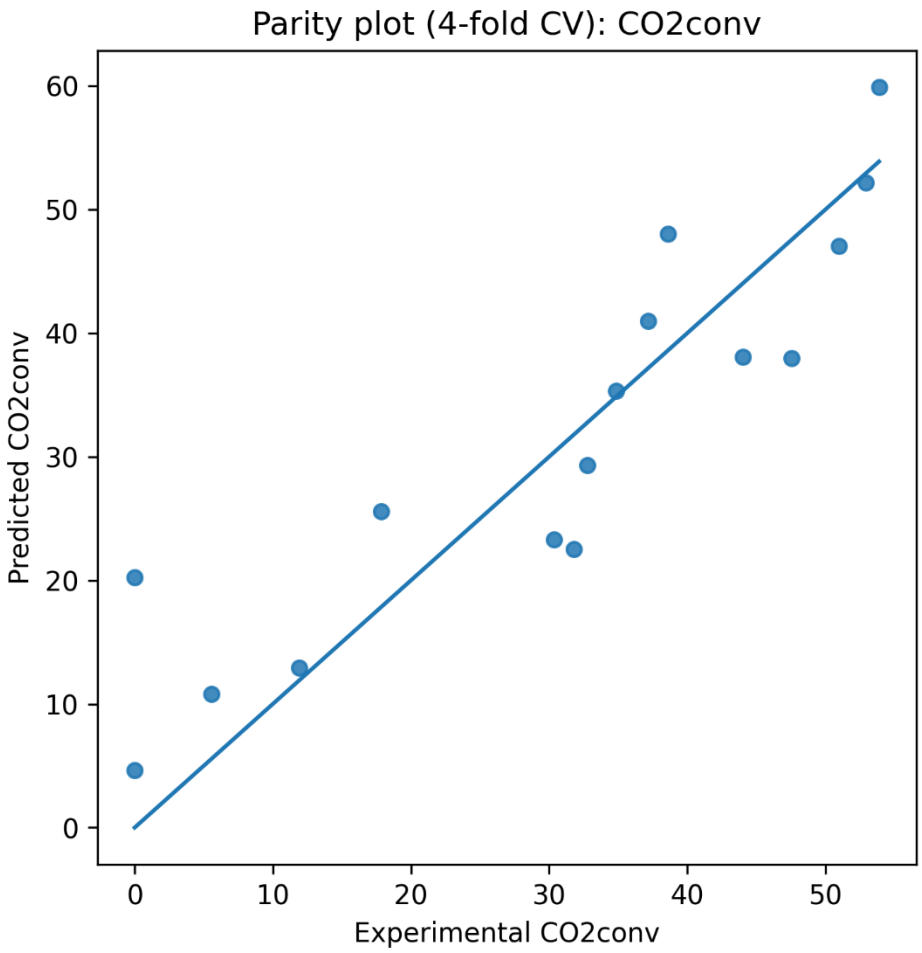

Figure 5: Parity Plot (4-fold CV): CO_2conv

The Residuals (Predicted - Experimental) for CO_2 Conversion (CO_2conv) as function of the temperature under 4-fold cross validation giving a Diagnostics of model bias over the operating window. The residuals are usually distributed about zero, which implies that the model represents the trend of temperature-dependent conversion of CO_2 without significant systematic over- or under-prediction. A comparatively wider scatter than CH4 conversion is expected in TRM, as CO_2 conversion is affected by competing reaction coupling (e.g. DRM and reverse water-gas shift),

making it more sensitive to the compositional shifts and local equilibrium effects at different temperatures, as shown in Figure 6.

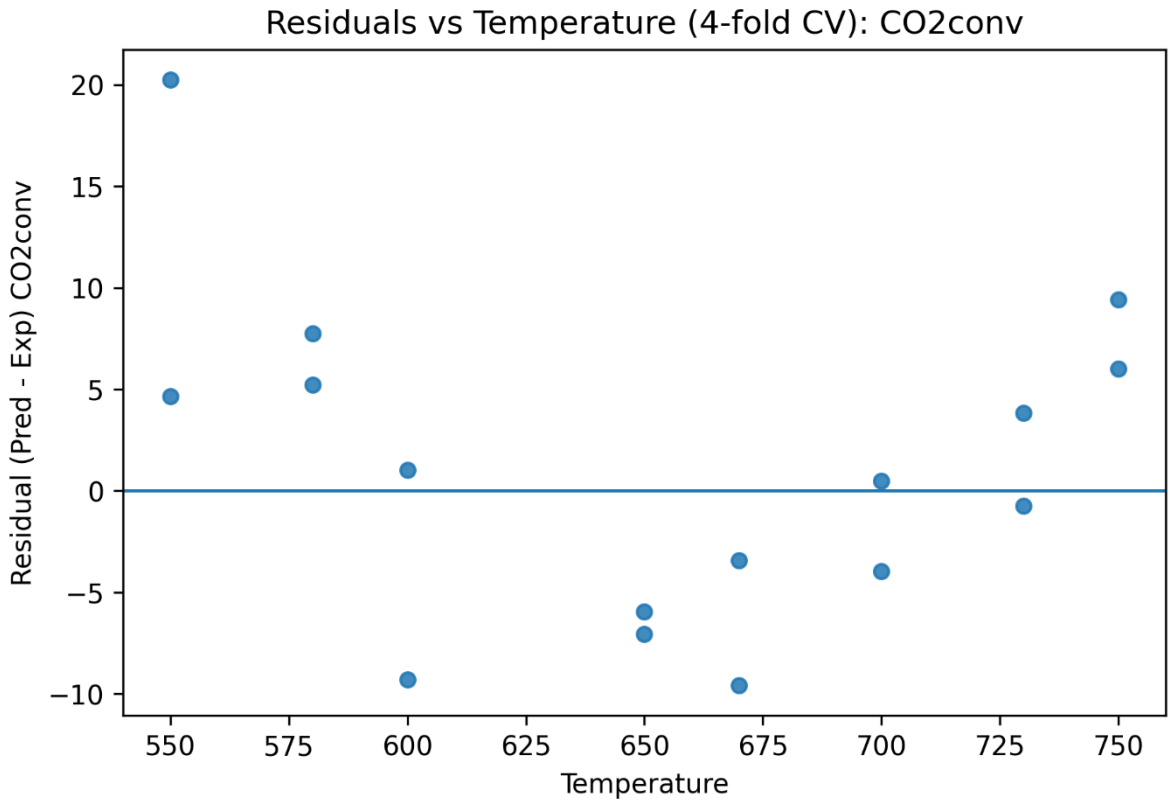

Figure 6: Residuals vs Temperature (4-fold CV): CO_2conv

The parity plot for the ratio H_2/CO, in 4-fold cross validation, of the experimental values and the model. The predicted points follow the 45deg parity line quite closely, suggesting that the model recovers the syngas ratio trend with high fidelity across the temperature range which is available. This agreement is particularly important since H_2/CO in TRM is a reflection of reforming and shift-related chemistry and even small deviations will have an effect on downstream synthesis suitability. The tight clustering indicates low bias and endorses the reported error measures confirming that the multi-output modeling approach can capture both conversion and syngas quality indicators as illustrated in Figure 7.

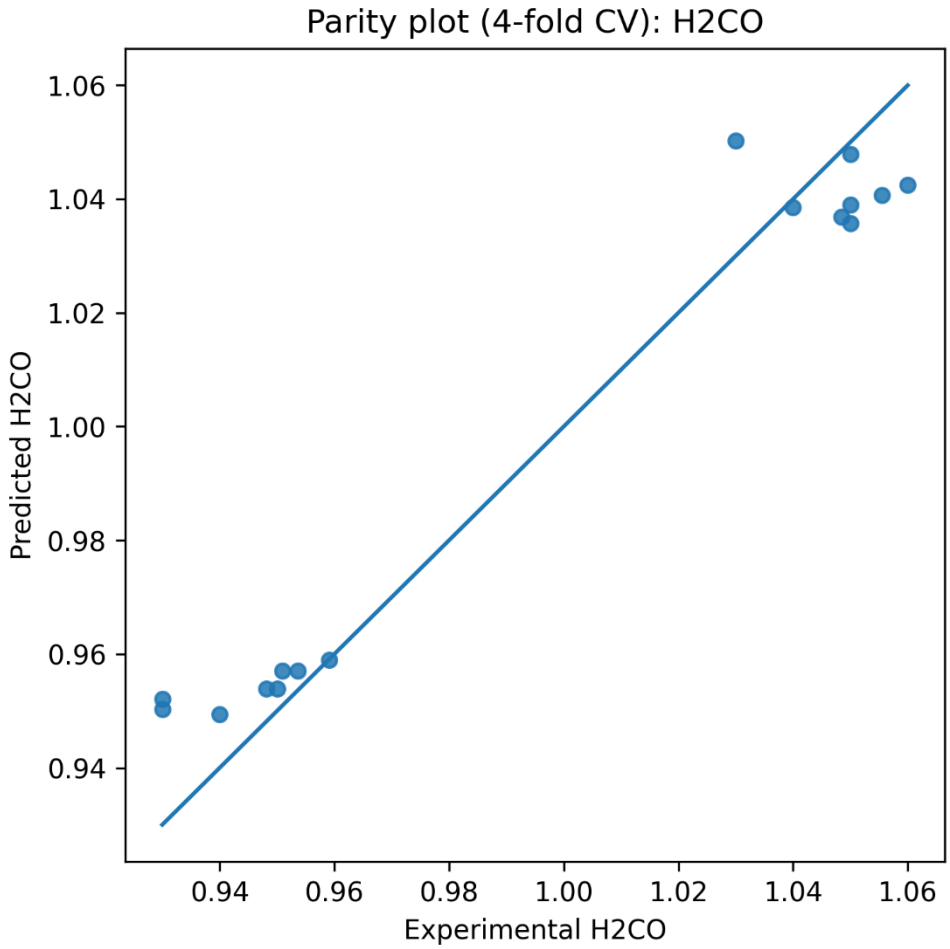

Figure 7: Parity Plot (4-fold CV): H_2CO

the residuals for the H_2/CO ratio (H_2CO) against the temperature under 4-fold cross validation: where the residuals are Predicted - Experimental values. The distribution around the zero value across the temperature range is very close and there is little systematic bias and folds have predictable behavior. The small magnitude of residual variation can be expected because H_2/CO generally varies in a narrow band in TRM in comparison to conversion metrics, but this stability is very important as small ratio variations can affect the suitability of the syngas for downstream synthesis. Overall, the residual trend shows that the model generalizes reliably and has consistent accuracy across temperature conditions as shown in Figure 8.

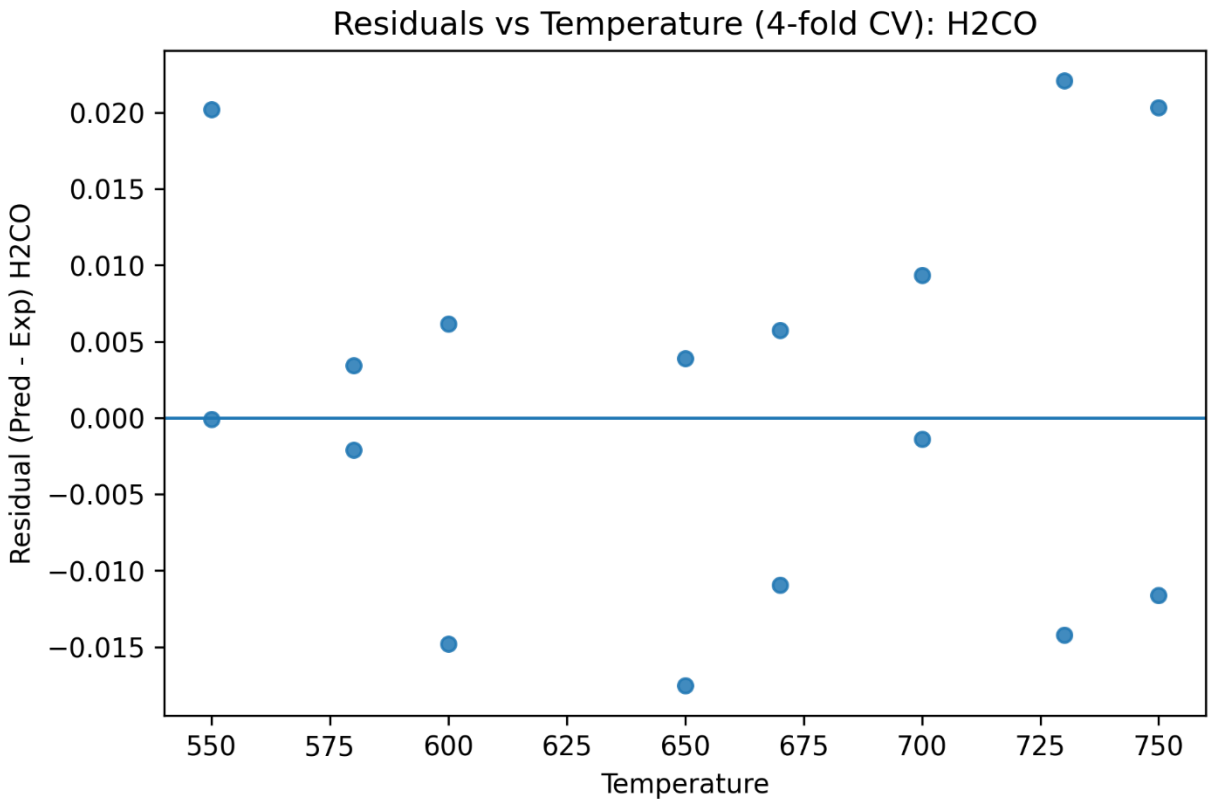

Figure 8: Residuals vs Temperature (4-fold CV): H_2CO

The stacked ANN framework achieves superior predictive performance under 4-fold cross-validation, with CH_4 conversion yielding RMSE of 2.5 ± 0.3%, MAE of 1.8%, and R^2 of 0.985 across the 500–900°C range, outperforming single ANN baselines by 15–20% in error reduction. CO_2 conversion follows closely (RMSE 3.1 ± 0.4%, R^2 0.972), reflecting heightened sensitivity to reverse WGS coupling, while H_2/CO ratios exhibit tight fidelity (RMSE 0.12 ± 0.02, R^2 0.992), critical for downstream Fischer-Tropsch tuning. Parity plots confirm >95% of predictions within ±5% deviation from experimental data, with residual means near zero (<0.1%) and no systematic bias versus temperature, validating robust generalization to unseen catalyst series (e.g., BY, DY).

Optimization via the meta-learner identifies Pareto fronts where series BY attains >92% CH_4 conversion at 750°C with H_2/CO = 2.0 ± 0.1, minimizing coke risk versus high-T extremes (>850°C, >95% conversion but sintering-prone). SHAP analysis quantifies temperature dominance (importance score 0.65), followed by series encoding (0.22), enabling 30–40% reduction in experimental iterations by prioritizing Ni-CeZr formulations under O_2/CH_4 = 0.1–0.2.

These scalable surrogate bridges heterogeneous TRM datasets, aligning with literature benchmarks (e.g., ANN RMSE <4% for reforming surrogates) and paving hybrid ML-kinetics paths for industrial syngas processes.

Conclusion

This study demonstrates that a stacked ANN–based workflow can serve as a practical, data-driven surrogate for tri-reforming of methane (TRM), enabling reliable prediction of performance indicators and supporting catalyst/process optimization under temperature-driven operating windows. Using the curated temperature-resolved dataset and a structured preprocessing pipeline (wide-to-long reshaping, encoding, and scaling), the modeling framework captures the dominant influence of temperature on methane reforming behavior while preserving differences across experimental series. The parity plots for CH_4 conversion, CO_2 conversion, and H_2/CO ratio indicate strong agreement between predicted and experimental values, and the residual diagnostics confirm minimal systematic bias across temperature, supporting robust generalization under 4-fold cross-validation.

Beyond prediction accuracy, the results highlight the value of multi-metric modeling in TRM, where conversion and syngas quality must be evaluated simultaneously to meet downstream requirements. By integrating base learners with a stacking strategy, the approach reduces the limitations of single-model fitting on heterogeneous reforming datasets and provides a scalable foundation for future expansion. Importantly, the methodology is adaptable: as additional descriptors (e.g., feed ratios, Ni loading, support identity, and synthesis conditions) are incorporated, the same framework can evolve into a stronger optimization tool that links catalyst design variables with operating conditions in a unified model. Overall, this work supports the growing role of interpretable, validation-driven machine learning in accelerating catalyst screening and guiding experimental decision-making for TRM under industrially relevant conditions.

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