Hybrid Neural Networks for Improved Chemical Process Modeling: Bridging Data-Driven Insights with Physical Consistency

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Abstract

The increasing reliance on neural networks (NN) in chemical process modeling highlights their capability for accurate predictions, yet their standalone application often struggles to adhere to fundamental physical laws such as equilibrium constraints and mass balance. Addressing this limitation, hybrid methods that integrate data-driven insights with physical consistency have gained prominence. This study investigates the integration of NNs with nonlinear data reconciliation (NDR), proposing it as a robust approach for enhancing the reliability of chemical process models. Using a Gibbs reactor as a case study and extending to reactor-distillation integration, we evaluate hybrid methodologies including NN x NDR, NN x KKT (Karush-Kuhn-Tucker), and KKT-PINN (Physics-Informed Neural Networks with KKT conditions). The proposed method of merging NNs with NDRs demonstrates superior performance in minimizing errors and enforcing physical constraints. Its robustness is validated under various conditions, showcasing scalability and applicability to multi-unit systems. This work underscores the transformative potential of hybrid approaches in achieving both data-driven accuracy and physical system fidelity.

Keywords: neural networks, nonlinear data reconciliation, karush-kuhn-tucker, unit operations.

1. Introduction

The integration of artificial intelligence, particularly neural networks (NNs), into process system engineering has significantly transformed the modeling landscape. Neural networks excel in capturing intricate, nonlinear relationships between inputs and outputs, making them invaluable tools for modeling complex phenomena in areas such as reaction kinetics, process optimization, and fault diagnosis. Unlike traditional equation-based models that rely heavily on detailed mechanistic understanding, NNs can learn directly from data, offering both flexibility and computational efficiency (Cavalcanti et al., 2021). These capabilities have led to their widespread adoption in chemical engineering, where they have been successfully employed to approximate reaction rate constants, optimize reactor performance, and design advanced control systems (Kiš and Klaučo, 2019). However, while their predictive accuracy is superior, their reliance on data alone often comes at the cost of physical fidelity—a limitation that becomes particularly pronounced in applications requiring strict adherence to fundamental principles like conservation of mass or energy. Standalone neural networks face several inherent challenges when applied to chemical processes. A critical issue is their inability to guarantee adherence to physical laws. Without explicit integration of constraints such as mass or energy balances, NNs may produce predictions that are scientifically implausible, undermining their reliability for process design and optimization. Moreover, the "black-box" nature of neural networks complicates their interpretability, limiting their acceptance in safety-critical industries that demand transparency and trust in predictive models (Schweidtmann et al., 2024). Another significant limitation arises from their reliance on extensive, high-quality datasets. In chemical engineering, where acquiring such data is often costly and time-consuming, NNs may perform poorly when trained on limited or noisy data, exhibiting poor generalization that makes them unsuitable for extrapolation or real-time decision-making.

Incorporating physical constraints into neural networks is crucial for addressing these limitations and enhancing their reliability. By embedding fundamental principles such as conservation laws and equilibrium conditions into the architecture or training process, models can generate predictions that are both accurate and physically consistent.

For instance, enforcing thermodynamic consistency ensures reliability in modeling complex systems, while reducing the risk of predictions that violate fundamental principles. Furthermore, the inclusion of physical constraints improves generalization and reduces the dependence on extensive datasets, allowing neural networks to perform robustly even with limited or noisy data. By integrating domain knowledge into neural networks, engineers can develop models that are not only computationally efficient but also interpretable and trustworthy, ensuring their applicability in designing and optimizing chemical processes (Chen et al., 2024).

To overcome these limitations, researchers have increasingly turned to hybrid modeling approaches that combine the strengths of data-driven techniques with first-principles knowledge. Hybrid models aim to bridge the gap between empirical and theoretical insights, enhancing the reliability, interpretability, and accuracy of process models (Ghosh et al., 2019). By embedding physical constraints directly into the modeling framework, hybrid approaches ensure that predictions align with established scientific principles. For example, physics-informed neural networks (PINNs) incorporate governing equations such as differential equations into the training process, guiding the learning algorithm to produce physically consistent results (Cuomo et al., 2022). Similarly, methods incorporating Karush-Kuhn-Tucker (KKT) conditions enforce equilibrium constraints during optimization, providing a means to embed critical process parameters directly into the neural network architecture (Lê, 2020). These developments represent a significant advance in process modeling, offering a promising pathway to address the limitations of standalone neural networks.

Despite the advancements achieved through hybrid models like those aforementioned, they still encounter significant challenges in the rigorous enforcement of physical constraints. While these methods incorporate physical laws such as governing differential equations or equilibrium conditions into the model's training process, they often fail to ensure strict adherence to these principles throughout the optimization and prediction phases. Specifically, existing hybrid models tend to rely on soft constraints, which allow for some degree of deviation from fundamental principles like mass and energy conservation, leading to predictions that, although physically plausible, may not fully respect the underlying laws.

In contrast, hard constraints, which enforce strict compliance with these laws, are less commonly integrated. This gap in enforcing hard constraints limits the reliability and physical fidelity of the models in real-world applications. Therefore, there is a clear need to target the bottleneck of the PSE community that is developing an approach that can seamlessly embed and enforce both soft and hard constraints, ensuring that predictions consistently adhere to fundamental physical principles without sacrificing computational efficiency while also taking into consideration the computational time and cost at stake.

Building on this foundation, and on the previous efforts done of merging neural networks with linear data reconciliation as a new hybrid methodology (Mousa et al., 2024), this study introduces a novel hybrid modeling approach that combines neural networks with nonlinear data reconciliation (NN x NDR). This method leverages the strengths of NDR, a mathematical technique for correcting raw data to enforce constraints such as mass and energy balances, to refine neural network predictions. Unlike existing approaches, NN x NDR operates by reconciling NN outputs post-prediction, ensuring strict adherence to physical laws without compromising computational efficiency. This modular approach addresses a critical gap in the existing hybrid modeling landscape, providing a robust framework for enhancing both the accuracy and reliability of neural network models in process engineering.
The novel NN x NDR method was tested on a Gibbs reactor, a system characterized by equilibrium constraints and nonlinear behaviors, making it an ideal case study for evaluating the efficacy and capabilities of our hybrid approach. By applying NN x NDR to predict reactor performance, the study ensured that outputs complied with equilibrium constraints while minimizing predictive errors. To benchmark its effectiveness, NN x NDR was compared to two established hybrid approaches: NN x KKT and KKT-HPINN. NN x KKT integrates KKT conditions directly into the training process, enforcing equilibrium constraints as hard conditions within the optimization algorithm. KKT-PINN, an advanced variant of PINNs, incorporates KKT conditions as intrinsic constraints within the network's architecture, ensuring that predictions adhere to physical principles. Both methods represent established strategies for combining data-driven and physics-based approaches, offering valuable points of comparison for the novel NN x NDR method. While each method has its advantages, the ability of NN x

NDR to achieve strict physical consistency without compromising computational efficiency makes it particularly well-suited for industrial applications. These findings underscore the transformative potential of hybrid approaches in chemical process modeling, bridging the gap between data-driven predictions and physical law fidelity.

To evaluate the robustness of NN x NDR, the method was subjected to a range of testing conditions that simulate real-world challenges in chemical process modeling. First, its ability to handle noisy data was assessed by introducing Gaussian noise into the training datasets, simulating scenarios where measurements are prone to errors. This evaluation tested the resilience of NN x NDR in maintaining accuracy and enforcing physical consistency under such conditions. Next, its performance under data scarcity was analyzed by progressively reducing the size of the training datasets. This test was critical in determining the model's ability to generalize when training data are limited—a common constraint in industrial applications. Finally, the scalability of NN x NDR was demonstrated through its application to a reactor-distillation integration process. This extended case study introduced additional complexities, such as mass balance and separation efficiency across interconnected units, providing a rigorous test of the model's ability to reconcile predictions across multi-unit systems. The results of this study will enable us to assess the significant advantages of NN x NDR in chemical process modeling as well as its ability to enforce physical constraints while maintaining high predictive accuracy, thereby possibly setting it apart from existing methods, offering a powerful tool for advancing process systems engineering.

This introduction lays the foundation for a comprehensive investigation into hybrid modeling strategies, positioning NN x NDR as a novel and promising approach. The subsequent sections will discuss the state of the art in hybrid modeling followed by a detailed explanation of the workings the hybrid, constraint enforcing, methodologies that will be used and tested in this article, along with the case studies applied and the results analysis.

2. State-of-the-Art and Contributions in Hybrid Modeling

The development of hybrid modeling techniques represents a critical innovation in computational science, addressing the limitations of standalone neural networks (NNs) by integrating physical laws, optimization techniques, and domain-specific constraints. These models emerged as a response to the growing complexity of systems requiring accurate predictions that also respect inherent physical laws. This section explores the evolution of hybrid models, their applications, and their limitations, building a case for the need for more robust approaches that enforce constraints while leveraging the predictive strengths of NNs.

Hybrid Modeling represents a significant evolution in the way we approach complex system modeling. Traditionally, models in computational science have been developed using either empirical models, which rely on data and observed patterns, or first-principles models, grounded in fundamental physical laws and theories. Each approach has its strengths and weaknesses: empirical models excel in prediction and handling vast amounts of data but struggle with generalization to new or unseen conditions. On the other hand, first-principles models provide a deeper, more mechanistic understanding of a system but can be computationally intensive and less effective in dealing with high-dimensional, nonlinear, and data-rich problems.

Hybrid Modeling is the fusion of these two paradigms, combining the best of both worlds as seen in Figure 1. It integrates empirical techniques which leverage data for pattern recognition with first-principles methods which provide the underlying scientific foundation of a system. This synergy enables hybrid models to not only offer robust, accurate predictions but also to scale and adapt to complex systems that would be difficult to model using either approach alone. In essence, hybrid models

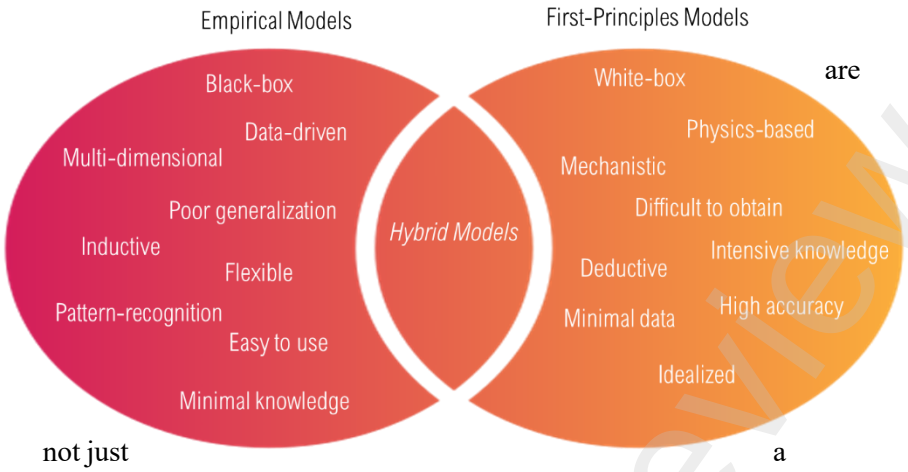


Figure 1 Venn diagram of hybrid models

are not just a computational advancement but a conceptual shift that allows for more flexible, efficient, and reliable modeling solutions for tackling real-world, dynamic challenges.

The push toward hybrid models has been fueled by advancements in computational power and the growing availability of data in domains such as engineering, climate science, and healthcare. By combining the predictive capabilities of machine learning with the physical interpretability of traditional models, hybrid approaches offer the best of both worlds. For instance, they can handle scenarios where first-principles methods alone would be insufficient due to system complexity or incomplete information, as well as those where machine learning models lack the ability to respect physical constraints.

2.1. Limitations of Standalone Neural Networks

While neural networks excel in tasks requiring pattern recognition and data-driven predictions, their limitations become apparent in domains where physical consistency and interpretability are critical. For example, in chemical engineering, standalone NNs have been used to predict reaction kinetics and system dynamics. However, certain studies have highlighted their inability to enforce conservation laws, often leading to physically unrealistic predictions (Giovannelli et al., 2023).

A significant limitation of neural networks (NNs) lies in their reliance on high-quality, abundant data. When faced with noisy or sparse datasets, NNs can produce erratic outputs. Furthermore, the "black-box" nature of these models complicates their application in fields like aerospace or medicine, where understanding causality and maintaining transparency are paramount. For instance, a study by (Nakamura-Zimmerer et al., 2022) noted that NNs used in flight control systems sometimes generated control actions that contradicted basic aerodynamic principles, highlighting the risks of unphysical behavior.

Another critical issue is overfitting, a common problem in neural networks, where models perform well on training data but fail to generalize to unseen conditions. A study by (Qiu et al., 2023) emphasized how overfitting can be particularly detrimental in predictive maintenance for industrial systems. When applied to fault detection, overfitting can lead to inaccurate predictions, such as missed fault detections or false alarms, both of which carry significant operational risks. In this context, hybrid approaches that combine deep learning with physical models could help address overfitting issues by improving generalization and robustness.

Moreover, standalone NNs lack the ability to incorporate domain-specific knowledge explicitly. While they can learn patterns from data, they cannot guarantee compliance with physical constraints, such as energy conservation or thermodynamic equilibrium. These limitations are particularly problematic in safety-critical systems, where violations of physical laws can have catastrophic consequences. From here, the need to address the limitations of solely using a neural network for system modeling has led to the emerging and evolution of hybrid modeling in various ways and types.

2.2. Evolution of Hybrid Modeling

Hybrid modeling has evolved as a response to the limitations of purely data-driven and first-principles approaches in complex system modeling. Early computational models were primarily based on empirical data-driven techniques, such as artificial neural networks (ANNs), which excel at capturing nonlinear relationships but lack interpretability and fail to enforce physical constraints (Psichogios and Ungar, 1992). Conversely, first-principles models, built on fundamental laws of physics and chemistry, provide interpretability but often struggle with scalability in high-dimensional systems (Pantelides and Renfro, 2013). The first significant advances in hybrid modeling emerged from process systems engineering (PSE), where researchers began integrating mechanistic models with machine learning techniques to enhance predictive accuracy while preserving physical realism (Schweidtmann et al., 2024). This evolution was further propelled by the development of Physics-Informed Neural Networks (PINNs), which embed governing equations into the loss function of NNs (Raissi et al., 2019), and Karush-Kuhn-Tucker (KKT)-based hybrid models, which incorporate optimization constraints to enforce equilibrium conditions (Chen et al., 2024). However, these models still struggle with balancing constraint enforcement and predictive flexibility.

Despite the advancements in hybrid modeling, research in this area remains highly active, with ongoing efforts to refine and extend existing methodologies. While existing methods have significantly improved constraint enforcement in neural network models, challenges persist in balancing predictive flexibility with strict adherence to physical laws. Some approaches focus on improving the scalability of hybrid models, enabling them to handle high-dimensional, complex systems more

efficiently (Krannichfeldt et al., 2024), while others explore alternative ways to embed physics-based constraints whilst having superior performance and accuracy (Blakseth et al., 2022). As hybrid modeling continues to evolve, the research community is actively investigating new frameworks that further integrate data-driven insights with rigorous physical principles, ensuring that models achieve both accuracy and reliability across diverse applications.

2.3. Types of Hybrid Modeling Approaches

Some of the most widely adopted hybrid modeling approaches include surrogate hybrid models, which use machine learning to approximate complex first-principles simulations (Fei et al., 2024), as well as ensemble hybrid models, which combine multiple learning-based and mechanistic models for improved robustness (Deng et al., 2023), and constraint-augmented hybrid models, where physical laws are embedded as soft or hard constraints during training (Ghosh et al., 2019).

While these methods have contributed significantly to bridging the gap between empirical and theoretical modeling, two particular hybrid approaches, that are PINNs and KKT-based models, have emerged as leading strategies for enforcing physical constraints in neural networks. Given their relevance to constrained optimization and physical law enforcement, and the fact that they will be used as benchmark-methods against our proposed hybrid approach, it is essential to explore them in greater detail where the following sections will delve into these frameworks.

2.3.1. Physics-Informed Neural Networks (PINNs)

Physics-Informed Neural Networks (PINNs) represent a significant advancement by embedding physical laws, expressed as partial differential equations (PDEs), into the NN training process. (Raissi et al., 2019) showcased PINNs in solving forward and inverse problems in fluid dynamics and heat transfer, demonstrating their ability to respect conservation laws while providing accurate predictions.

However, PINNs face inherent challenges. One notable limitation is the compromise between predictive accuracy and constraint enforcement. By treating physical constraints as soft penalties in the loss function, PINNs may achieve suboptimal adherence to these constraints, especially in systems with stiff or nonlinear dynamics. This trade-off often requires extensive hyperparameter tuning, as reported by (Escapil-Inchauspé and Ruz, 2023). Furthermore, the computational burden of enforcing constraints grows significantly in high-dimensional or large-scale problems, limiting the practicality of PINNs in industrial applications.

2.3.2. Karush-Kuhn-Tucker (KKT)-Based Hybrid Models

The Karush-Kuhn-Tucker (KKT) conditions, fundamental to constrained optimization, have been integrated into hybrid models to enforce equilibrium constraints. These models are particularly valuable in chemical process optimization, where thermodynamic laws must be upheld. These models leverage the KKT framework to ensure solutions remain consistent with system constraints under varying operational conditions.

Despite their strengths, KKT-based models have limitations and challenges. One notable limitation is their reliance on gradient-based optimization methods, which are inherently susceptible to convergence toward suboptimal solutions, particularly in non-convex problem domains. This issue is exacerbated in complex bi-level optimization scenarios, where the integration of KKT conditions further complicates the optimization landscape.

Recent studies, such as that of (Moghaddas and Tohidi, 2020), have emphasized these challenges, highlighting the critical need for advanced methodologies that can effectively navigate the trade-offs between solution accuracy and computational feasibility. Additionally, the computational overhead of integrating KKT conditions into NN training can hinder scalability, particularly in applications involving real-time decision-making (Femine, 2024).

Accordingly, accurate initialization and precise constraint formulation are often emphasized as critical to avoid convergence issues and ensure feasible solutions. Nevertheless, KKT-based hybrids offer a systematic approach to constrained optimization, therefore addressing these

computational and convergence challenges is essential for their effective application in complex systems.

In a nutshell, the limitations of existing hybrid models underscore the need for methodologies that aim to integrate hard constraints with the predictive power of NNs. Current approaches often trade-off between fidelity to physical laws and data-driven accuracy, resulting in models that are either too rigid or insufficiently constrained. For example, while PINNs excel in enforcing soft constraints, their predictive accuracy can suffer under complex physical systems. Conversely, KKT-based methods ensure strict adherence to constraints but lack adaptability and scalability.

Thereby a unified framework that effectively integrates the strengths of existing hybrid modeling approaches is indispensable for addressing the limitations identified in current methodologies. Such a framework would prioritize the enforcement of hard constraints, ensuring strict adherence to physical laws, while simultaneously leveraging the flexibility and adaptability of neural networks (NNs) for accurate pattern recognition and predictive modeling. By bridging the gap between the rigidity of traditional physical models and the adaptability of data-driven approaches, this framework ought to have the potential to achieve an optimal balance between fidelity and generalizability.

This study seeks to contribute to this vision by exploring and refining advanced hybrid modeling methodologies. Through a systematic examination of emerging techniques and their limitations, the research aims to develop a novel framework that address scalability, computational efficiency, and constraint adherence. The outcomes are expected to pave the way for innovative and robust hybrid models capable of meeting the multifaceted demands of modern engineering and scientific challenges. These contributions will not only enhance predictive performance but also establish a solid foundation for extending these methodologies across diverse industrial and research applications.

3. Hybrid Frameworks for Constraint Compliance

In complex systems, achieving accurate predictions while adhering to physical constraints is a significant challenge. In this study, we propose different hybrid approaches firstly by combining neural networks with

nonlinear data reconciliation, followed by integrating optimization techniques based on the Karush-Kuhn-Tucker (KKT) conditions, and then by embedding KKT-based constraints within physics-informed neural networks (PINNs). These methodologies aim to address the limitations of standalone data-driven models, ensuring predictions that are both accurate and physically consistent.

3.1. Neural Network x Linear and Nonlinear Data Reconciliation

Data reconciliation (DR) is a statistical technique designed to improve the accuracy and consistency of measured process data. Measurements collected from real-world systems often contain noise, inaccuracies, or inconsistencies due to instrument errors, process disturbances, or environmental factors (Kelly, 2004). DR addresses these limitations by adjusting raw data to align with known physical and operational constraints, such as mass and energy balances or thermodynamic principles. This ensures that the reconciled data reflects both statistical reliability and physical validity.

Traditional DR methods are rooted in linear systems and rely on the assumption that process relationships can be described using linear constraints. Linear DR focuses on minimizing discrepancies between measured and reconciled values while satisfying linear constraints, making it computationally efficient. However, while effective for simple systems, linear DR cannot handle the complexities of many real-world systems, where nonlinear relationships dominate. For example, chemical reactions, thermodynamic equilibria, and fluid dynamics often involve nonlinear phenomena governing the system to be studied. Accordingly, in such cases, a more sophisticated approach is considered, that is Nonlinear Data Reconciliation (NDR).

While linear DR operates within a simplified optimization framework that assumes linear relationships between variables, NDR incorporates the much broader and more challenging domain of nonlinear equality or inequality constraints into the reconciliation process.

In essence, NDR formulates the reconciliation process as a constrained nonlinear optimization problem. The primary objective is to adjust the measured data, which may contain noise or inaccuracies, so that the reconciled values not only minimize deviations from the observed data but also strictly comply with the system's nonlinear physical laws. Unlike linear DR, where constraints can be expressed as straightforward linear equations (e.g., mass or energy balance), NDR accommodates nonlinear relationships which are often expressed as highly nonlinear functions of the system variables (Cencic, 2016). To achieve this, it employs advanced numerical optimization techniques that iteratively adjust reconciled values until convergence (Tian et al., 2006). By balancing measurement corrections with adherence to nonlinear constraints, NDR delivers reconciled data that is both statistically accurate and physically meaningful.

This merge between NN and NDR is grounded in the sense that the neural network acts as a soft sensor, generating initial predictions that approximate the system's behavior. Nonlinear data reconciliation then refines these predictions by enforcing hard physical constraints, ensuring that the reconciled data is both accurate and consistent with physical laws. However, it’s important to keep an eye on the computational time of the system to assess its feasibility.

This integration transforms the NN from a purely data-driven model into a physics-informed hybrid model. By reconciling the NN’s outputs, NN x NDR not only would aim to improve predictive accuracy but also to ensure that the predictions adhere to domain knowledge. It also involves a systematic workflow designed to combine the predictive power of NNs with the physical rigor of NDR. Accordingly, the following steps outline the methodology employed to achieve accurate, constraint-compliant reconciled data.

Step 1: Neural Network Predictions

The process begins with the design and training of a neural network (NN) to predict key system variables based on a given data set. The NN architecture is chosen to accurately capture the system's nonlinear behavior, incorporating an appropriate number of layers,

nodes, and activation functions. Additionally, dropout regularization layers are introduced to mitigate overfitting and improve generalization by preventing the network from relying too heavily on specific neurons and by targeting the uncertainty distribution. Once trained, the NN is used as a soft sensor to generate predictions for the system's variables. To account for uncertainties in the NN's predictions, multiple runs are performed with varying initializations (for ex. different random seeds), producing an ensemble of predictions.

Step 2: Data Segmentation and Statistical Analysis of NN Predictions

The ensemble of the network's predictions is segmented into smaller subsets to ensure that the reconciliation process accounts for localized system behaviors and variations. Then, the mean vector (X_{an}) and the covariance matrix (V) for each subset are computed (Eq.1 & Eq.2). These statistical metrics provide a robust representation of the predicted values and their associated uncertainties:

$$X_{an} = \frac{1}{N}\sum_{i=1}^{N} x_i \quad (1)$$

$$V = \frac{1}{N-1}\sum_{i=1}^{N} (x_i - X_{an})(x_i - X_{an})^T \quad (2)$$

Where N is the number of predictions, and x_i represents the predicted values from the i-th initialization. These statistics provide the foundation for NDR, quantifying the variability and central tendency of the neural network's predictions.

Step 3: Formulation of the Objective Function

The core of the reconciliation process revolves around minimizing a constrained objective function (Eq.3) that resembles the discrepancies between the reconciled variables x and the inaccurate predictions:

$$y(x) = \frac{1}{2}(x - X_{an})^T V^{-1}(x - X_{an}) + p(x) \quad (3)$$

$$p(x) = \sum log\,(1 + |x_{reconciled} - X_{an}|) \quad (4)$$

Where the first term represents the weighted squares error that measures and minimizes the differences between the reconciled values (x) and the NN-derived mean values (X_{an}). While the second term (p(x)) is a penalty function that introduces a logarithmic barrier to constraint violations, ensuring a smoother and more stable optimization process. The logarithmic growth of this term allows the system to prioritize reducing large constraint violations while remaining less sensitive to minor errors, thereby preventing overcorrection and ensuring a balanced reconciliation that maintains physical consistency without unnecessary rigidity.

Step 4: Definition of Nonlinear Constraints

The constraints (z(x)) are derived from the fundamental physical or operational laws governing the system, expressed as nonlinear equality or inequality functions. These constraints ensure that the reconciled values comply with system requirements, such as conservation principles, equilibrium relationships, or other governing dynamics. An example of such a constraint can be expressed as:

$$z(x) = \prod_i x_i^{a_i} - \prod_j x_j^{b_j} = 0 \quad (5)$$

Here, x_i and x_j are the reconciled variables, while a_i and b_j are coefficients that define the relationship between the variables, often determined by stoichiometric or system-specific properties.

For example, this form can represent a generalized thermodynamic equilibrium constraint such as:

$$K_{eq} = \frac{\prod_i c_i^{v_i}}{\prod_j c_j^{v_j}} \quad (6)$$

Step 5: Optimization and Reconciliation

After computing the variables' mean (X_{an}) and variance (V) values, then defining the physical constraints (z(x)) to be enforced, followed by introducing the objective function (y(x)) to be minimized, it's time to start the reconciliation process. This step employs an advanced numerical optimization algorithm, such as Sequential Least Squares Quadratic Programming (SLSQP), to solve the constrained optimization problem. This algorithm iteratively adjusts the

reconciled variables (x) to minimize the objective function while satisfying the nonlinear constraints.

In conclusion, the NN x NDR methodology represents a significant advancement in the world of hybrid modeling, offering a novel solution that combines the power of machine learning with the enforcement of physical constraints. Without doubting the fact that the NN x NDR approach stands as the core contribution of this study, the subsequent methodologies will be employed to validate its superior performance and further benchmark its effectiveness against other constraint-enforcing techniques.

3.2. Neural Network x Karush-Kuhn-Tucker

The Karush-Kuhn-Tucker (KKT) conditions are a set of necessary conditions for a solution to be optimal in a constrained optimization problem, particularly in cases where the objective function and the constraints are nonlinear. These conditions are fundamental in optimization theory, especially in the context of problems involving inequality and equality constraints (Ghojogh et al., 2021). The KKT conditions extend the concept of Lagrange multipliers to handle more complex optimization scenarios.

3.2.1. Key Concepts of Karush-Kuhn-Tucker

To fully grasp the utility and application of the Karush-Kuhn-Tucker (KKT) conditions in constrained optimization problems, it is essential to understand their foundational concepts. The KKT framework not only provides a mathematical basis for solving optimization problems with nonlinear constraints but also establishes necessary criteria for determining optimal solutions. Below, we outline the key components of the KKT methodology, highlighting their relevance and role in achieving physically consistent and optimal results (Kuhn and Tucker, 1951).

1. Optimization Problem:

The general form of a constrained optimization problem is:

$$\text{Minimize } f(x)$$

$$g_i(x) \leq 0, \qquad i = 1,\ldots,m \tag{7}$$

$$h_j\ (x) = 0, \qquad j = 1,\ldots,p \tag{8}$$

where $f(x)$ is the objective function, $g_i(x)$ are the inequality constraints, and $h_j(x)$ are the equality constraints.

2. *Lagrange Multipliers* :

The KKT conditions introduce Lagrange multipliers (λ for inequality constraints and μ for equality constraints) to incorporate the constraints into the optimization process.

The Lagrangian function L is defined as:

$$L(x,\lambda,\mu) = f(x) + \sum_{i=1}^{m} \lambda_i \,.g_i(x) + \sum_{j=1}^{p} \mu_j \,.\, h_j(x) \tag{9}$$

3. *KKT Conditions*:

The KKT conditions consist of:

- *Stationarity*: The gradient of the Lagrangian with respect to x should be zero. It indicates that at the optimal point, the direction of improvement in the objective function must be balanced by the constraints' directions (via multipliers).

$$\nabla_x L(x,\lambda,\mu) = 0 \tag{10}$$

- *Primal Feasibility*: The original constraints must hold to ensure that the solution respects the constraints.

$$g_i(x) \leq 0, \qquad h_j\ (x) = 0 \tag{11}$$

- *Dual Feasibility*: The Lagrange multipliers for inequality constraints must be non-negative which aligns with the economic interpretation of constraints.

$$\lambda_i \geq 0 \tag{12}$$

- *Complementary Slackness*: For each inequality constraint, the product of the Lagrange multiplier and the constraint must equal zero which in terms indicates that non-active constraints do not influence the solution, while active constraints do.

$$\lambda_i \quad .g_i(x) = 0 \tag{13}$$

In summary, the Karush-Kuhn-Tucker conditions provide a robust framework for enforcing constraints in optimization problems, therefore leveraging their principles with neural networks shall enable a hybrid approach that ought to ensure accurate and physically consistent solutions.

3.2.2. Synergizing KKT principles with Neural Networks

The integration of Karush-Kuhn-Tucker (KKT) conditions with neural networks offers substantial advantages, particularly when modeling systems governed by physical laws and constraints. Below are the key benefits of incorporating KKT-inspired techniques into neural networks (Arvind et al., 2024; Femine, 2024):

1. ***Ensuring Physical Validity*:** Traditional neural networks are designed to optimize a loss function based on training data but often lack mechanisms to enforce underlying physical constraints. By embedding KKT conditions into the network's optimization process, these constraints are directly incorporated, ensuring that predictions remain physically consistent. For example, equilibrium constants in chemical reactors, such as those in Gibbs systems, can be maintained reliably through the KKT framework.

2. ***Enhanced Generalization:*** Integrating physical laws as constraints allows neural networks to extend beyond data-driven predictions, leveraging domain-specific knowledge to prevent overfitting. This results in more robust models that can generalize effectively to unseen data, improving predictive reliability in diverse scenarios.

3. ***Optimization Efficiency:*** KKT conditions, derived from constrained optimization theory, introduce a structured approach to handling constraints. Rather than solely minimizing a loss function, the neural network aligns its predictions with physical expectations by simultaneously satisfying equilibrium or other system-specific

conditions. This synergy ensures an efficient training process and optimally constrained solutions.

4. ***Reliable Predictions:*** In critical applications, such as chemical engineering, the accuracy and reliability of predictions are paramount. By enforcing physical properties, the KKT approach reduces the risk of generating unrealistic or physically infeasible outputs, fostering greater confidence in the model's predictions.

Traditional KKT methods address constrained optimization problems by introducing Lagrange multipliers, which quantify the importance of satisfying constraints while optimizing an objective function. This integration of theoretical rigor with neural network methodologies creates a powerful framework for tackling complex, constraint-driven modeling challenges.

In this approach, a similar philosophy is adopted, where the neural network is trained to predict the output variables, but an additional mechanism is employed to integrate the constraints into the network's predictions. Rather than explicitly formulating a Lagrangian function, a correction factor is introduced that dynamically adjusts the predicted outputs to ensure compliance with the required physical constraint. This correction mechnism mirrors the role of Lagrange multipliers in traditional KKT, acting as a dynamic adjustment to align the model's outputs with imposed physical laws.

The methodology employs a projection-based correction mechanism to enforce the physical constraint, implemented as follows:

1. ***Prediction of Outputs:***
   The neural network is trained to predict output variables, denoted as $\hat{y}$, representing the predicted values for each system variable. These initial predictions, however, may not inherently satisfy the physical constraint in question.
2. ***Computation of the Required Physical Constraint:***
   Based on the predicted outputs, the physical constraint that needs to be enforced is calculated. To keep consistency with the constraint taken as an example in NN x NDR, the equilibrium constant can be considered as

the physical constraint in this section as well, and it is determined from the predicted variables as in:

$$K_{eq,predicted} = \frac{\prod^{i \in N_{num}} (\hat{y}_i)^{p_i}}{\prod^{j \in N_{den}} (\hat{y}_j)^{q_j}} \quad (14)$$

Where:

- N_{num} and N_{den} are the sets of indices corresponding to the numerator and denominator of the equilibrium equation.
- p_i and q_j are the respective exponents for each $\hat{y}_i$ and $\hat{y}_j$ in the equation.

3. ***Reference Value for the Physical Constraint:***
   The target or actual value of the physical constraint, such as the equilibrium constant ($K_{eq,\,actual}$), is obtained from reference data, experimental observations, or validated simulations.

4. ***Computation of the Scaling Factor:***
   A scaling factor, α, is determined to adjust the predicted outputs such that the physical constraint is satisfied. This factor is calculated as:

$$\alpha = \left(\frac{K_{eq,\,actual}}{K_{eq,predicted}}\right)^{\frac{1}{n}} \quad (15)$$

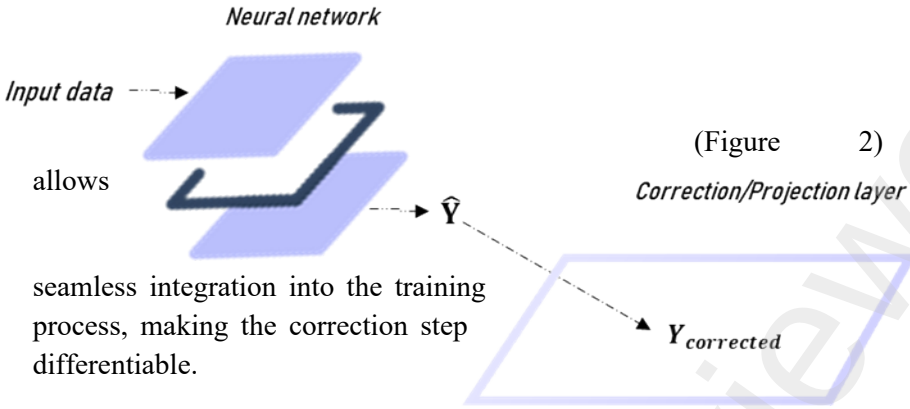
Where n is the sum of the exponents in the constraint equation:

$$n = \sum_{i \in N_{num}} p_i + \sum_{j \in N_{den}} q_j \quad (16)$$

5. ***Applying the Correction:***
   The scaling factor is then applied to the predicted outputs to produce the final corrected outputs:

$$y_{corrected} = \alpha \,.\, \hat{y} \quad (17)$$

This correction process happens in the form of projecting the predicted output to the desired, physically consistent, output; and it is integrated directly into the neural network architecture as a custom constraint correction layer. By functioning as a specific layer within the network, the correction mechanism adjusts the predictions after they are generated, ensuring they satisfy the equilibrium constant conditions. This setup



(Figure 2) allows seamless integration into the training process, making the correction step differentiable.

Figure 2 Integrating neural networks with KKT inspired constraints for optimized predictions

While traditional KKT optimization explicitly uses Lagrange multipliers to combine the objective function and constraints into a single optimization problem, this methodology adopts a more implicit yet effective approach. Rather than forming a combined objective, the neural network outputs are dynamically adjusted after prediction through a KKT-inspired correction layer. This ensures that the neural network learns to predict outcomes that are not only accurate but also feasible within the physical constraints of the system, similar to how KKT finds solutions that are feasible and optimal.

The projection mechanism serves as an analog to the classical approach of finding stationary points of a Lagrangian. It ensures the outputs are projected into a valid, physically consistent space, mirroring the process by which KKT conditions maintain feasibility and optimality. By doing so, the methodology achieves a balance between data-driven learning and the enforcement of known physical laws, a key advantage of combining neural networks with KKT-inspired principles.

3.3. Karush-Kuhn-Tucker x Physics-Informed Neural Network

To further evaluate the coupling of KKT principles with neural networks against our proposed methodology of merging nonlinear data reconciliation (NDR) with neural networks, the architecture of the neural network was modified to develop a physics-informed neural network (PINN). This adaptation led to a KKT-PINN model, where the physical constraint was more deeply embedded within the loss function of the neural network. The methodology's objective is to try and to draw on the strengths of both KKT optimization and PINNs by observing the efficacy level of enforcing physical feasibility via the custom loss function and optimizing the neural network's parameters through KKT's constrained optimization. This integration overthrows the standard PINNs that impose physical constraints as soft penalties in the loss function due to the fact that the change in the network is not only merely in the loss function, but also in having a KKT-inspired custom constraint layer to ensure strict constraint-compliance. Therefore, we are combining the flexibility of PINNs with the rigorous constraint enforcement of KKT.

The loss function in KKT-PINN combines traditional data-driven loss terms with the necessary constraints imposed by the KKT conditions, which helps the network learn both the empirical relationships from the data and the underlying physics governing the system. Specifically, the KKT-PINN loss function includes several key components:

1. ***Data Loss Term (Empirical Loss):***
   The first component of the loss function is the traditional empirical loss term, which measures how well the model fits the observed data. This is typically a mean squared error (MSE) between the predicted outputs and the actual observed data:

$$L_{data} = \frac{1}{N}\sum_{i=1}^{N} (\hat{y_i} - y_i)^2 \quad (18)$$

   Where:
   - $\hat{y_i}$ is the predicted output
   - y_i is the true observed value
   - N is the number of data points

2. ***Physical Constraint Term (PINN Loss):***
   The second term incorporates the physical constraint directly into the loss function. For instance, in a system governed by an equilibrium condition, this term might be designed to penalize the network if its predictions deviate from the expected physical law. Using the equilibrium constant as an example, the constraint can be formulated as:

$$L_{constraint} = |K_{eq,predicted} - K_{eq,actual}|^2 \quad (19)$$

   Where:
   - $K_{eq,predicted}$ is the equilibrium constant calculated from the network's predicted outputs
   - $K_{eq,actual}$ is the reference or known equilibrium constant based on experimental or simulated data.
   - This term ensures that the neural network predictions not only fit the data but also respect the physical law governing the system.

To conclude this section, we have introduced a set of hybrid frameworks aimed at addressing the challenges of achieving accurate predictions while ensuring adherence to fundamental physical and operational constraints. These methodologies integrate data-driven approaches with constraint-enforcing principles, leveraging the synergy between predictive capabilities and the preservation of system integrity. By

embedding domain knowledge into modeling frameworks, they provide a pathway for reconciling the flexibility of machine learning with the rigor of physical laws.

The subsequent section will focus on the application of these methods to a specific case study, providing a critical evaluation of their performance, specifically our proposed novel approach, against each other.

4. Case Study and Results

This case study examines a Gibbs reactor performing the incomplete hydrogenation of toluene, producing methane, benzene, and biphenyl as reaction products. The system's behavior is governed by the equilibrium constant, a fundamental physical constraint ensuring thermodynamic consistency.

The neural network architecture employed in this study is consistent throughout all the applications and the scope of this article and it consists of four layers: an input layer, two hidden layers, and an output layer. Each hidden layer comprises 128 neurons with the ReLU activation function. Also, to account for uncertainty in the model's predictions, dropout layers of 20% probability were incorporated. By randomly deactivating neurons during training, dropout prevents overfitting and improves generalization.

The input features include key reactor operating conditions, such as the feed flow rates of toluene and hydrogen, along with temperature and pressure. The network is trained to predict the reactor's outlet flow rates, corresponding to methane, benzene, and biphenyl. A dataset of 2,000 points, divided into 80% for training and 20% for testing, is simulated via ProSim and is used to build and evaluate the model.

With prior knowledge that the neural network generates initial predictions of the outlet flow rates, based on the input condition, that are purely data-driven and do not inherently satisfy the equilibrium constraint, the following parts will discuss the employment of the aforementioned hybrid approaches to test their performance in the equilibrium constraint enforcement.

4.1. NN x NDR

In the reactor context, this approach ensures that predictions align with thermodynamic laws, specifically the equilibrium constant (Keq). As detailed earlier, step 4 of the reconciliation process incorporates a nonlinear constraint to ensure adherence to thermodynamic consistency. This constraint in this case is expressed as:

$$K_{eq}.(x_2{}^2.x_5{}^3) = (x_3{}^3.x_4.x_6) \quad (20)$$

Where x_2, x_3, x_4, x_5, x_6 are the reconciled concentrations of methane, benzene, biphenyl, toluene, and hydrogen, respectively. By

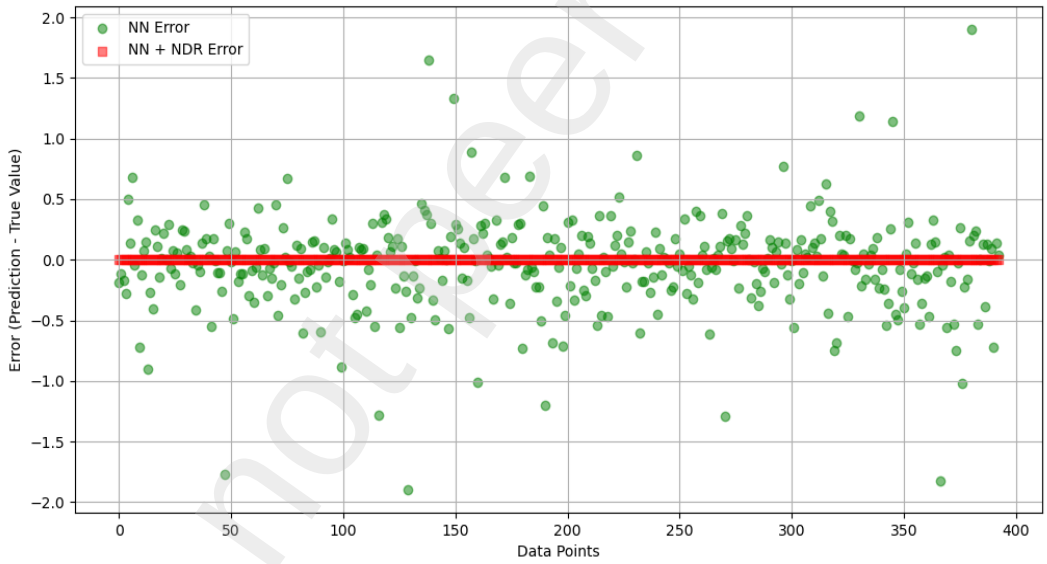


Figure 3 Scatter plot of the prediction errors of Keq between NN and NN-NDR against true desired values

NDR model refines the predictions to ensure they comply with the equilibrium law governing the chemical system (while mass balance of the system always hold true).

Figure 3 compares the prediction errors for Keq between the standalone neural network and the NN x NDR hybrid framework. The error associated with the standalone NN is both substantial and oscillatory, fluctuating around the true equilibrium constant. These fluctuations highlight the NN's inability to inherently satisfy

thermodynamic constraints. This shortcoming stems from the NN's optimization objective, which focuses solely on minimizing statistical error in the training data. Without explicit consideration of physical constraints, the NN is free to generate predictions that may statistically minimize error but deviate from thermodynamic consistency. Consequently, the NN's predictions are prone to inaccuracies that undermine their reliability in modeling physically constrained systems.

In contrast, the NN x NDR model demonstrates markedly improved performance. By integrating the nonlinear reconciliation step into the prediction process, this framework corrects the NN's initial outputs to ensure compliance with the equilibrium constant. The reconciled predictions exhibit zero error, as shown in Figure 4, effectively bridging the gap between data-driven accuracy and physical validity. This improvement underscores the role of NDR as a corrective mechanism that enforces adherence to the underlying thermodynamic laws.

The superiority of the NN x NDR framework lies in its dual optimization strategy, which balances statistical accuracy with adherence to physical constraints. The nonlinear reconciliation step, governed by the equilibrium constant equation, minimizes deviations from both the neural network's predictions and the thermodynamic laws. This ensures that the final reconciled outputs are not only accurate with respect to the data but also consistent with the fundamental principles governing the system. Additionally, one of the key advantages of this approach lies in its minimal computational overhead making it virtually non-existent in terms of processing burden. By embedding these constraints directly into the modeling process, the NN x NDR framework achieves a level of reliability that standalone data-driven models cannot match in physically constrained systems, ensuring reliable and valid predictions. Therefore, comparing this method to alternative frameworks can further validate its efficacy and demonstrate its applicability to a broader range of complex systems.

4.2. NN x KKT

To assess the effectiveness of the NN x NDR hybrid approach, its performance is benchmarked against another prominent hybrid methodology, the NN x KKT framework.

The NN x KKT method modifies the neural network's training process to incorporate the physical constraints directly into its optimization objective. By embedding the equilibrium constant as a hard constraint within the optimization process, the NN x KKT approach ensures that predictions align more closely with thermodynamic principles while maintaining the flexibility of neural network-based predictions. This integration reshapes the solution space, ensuring that the network

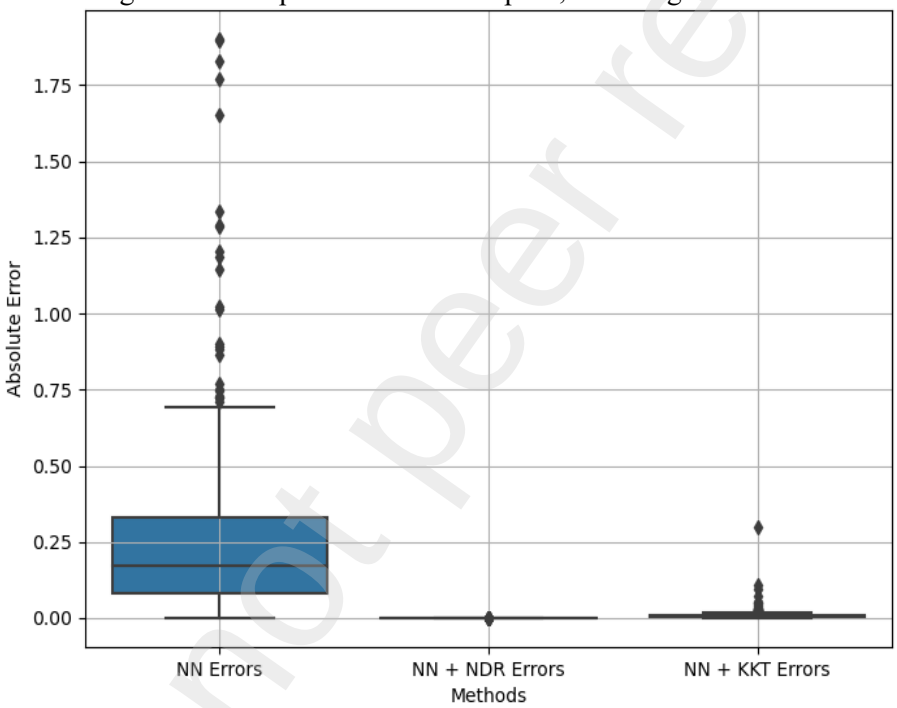


Figure 4 Error distribution of the 3 different methods against the desired output.

outputs adhere to the equilibrium constant constraint. However, this adherence depends on the success of the optimization algorithm in achieving convergence within the constrained domain.

The NN x KKT framework demonstrates its ability to produce predictions that align reasonably well with the desired equilibrium constant. As shown in Figure 4, the corrected predictions show a significant reduction in error compared to a standalone neural network, effectively mitigating the large oscillatory deviations observed in unconstrained data-driven models. By embedding the physical

constraint into the training process, the NN x KKT method restricts the solution space to thermodynamically valid outputs, representing a meaningful improvement over the unconstrained neural network with minimal computational time.

However, the NN x KKT approach is not without limitations. While it enforces physical consistency, minor deviations from the true equilibrium constant persist. These discrepancies arise due to challenges in the optimization process, particularly when the model must balance data-driven accuracy with strict adherence to the constraint. In scenarios where the optimization landscape is complex, convergence may stall, resulting in residual errors. Although these errors are small, they underscore the trade-off between enforcing constraints and ensuring precise data fitting. In contrast, the NN x NDR hybrid approach achieves superior performance. By decoupling the prediction and reconciliation processes, it avoids the optimization challenges faced by the NN x KKT method. The two-step workflow of the NN x NDR framework first produces initial predictions using a neural network and subsequently refines them through nonlinear data reconciliation (NDR). This reconciliation process minimizes deviations from both the physical constraints and the initial data, yielding predictions that perfectly match the true equilibrium constant. The result is a zero-error outcome, as evidenced in Figure 5, which showcases the NN x NDR framework's ability to fully reconcile data-driven predictions with physical laws.

4.3. KKT x PINN

Building upon the integration of KKT principles with neural networks, there is growing interest in exploring whether enhancing the neural network with physics-informed capabilities could yield superior results. The transition to a KKT x PINN framework embeds the physical constraint more deeply into the neural network by incorporating it directly into the loss function. This approach aims to simultaneously capture complex data-driven patterns and enforce physical constraints more rigorously, potentially addressing the minor residual errors observed in the NN x KKT method. In the KKT x PINN framework, the architecture of the neural network is adapted to a physics-informed neural network (PINN), where the loss function is designed to balance a data-driven error term with a residual term representing the physical constraints, as mentioned in section 3.3.

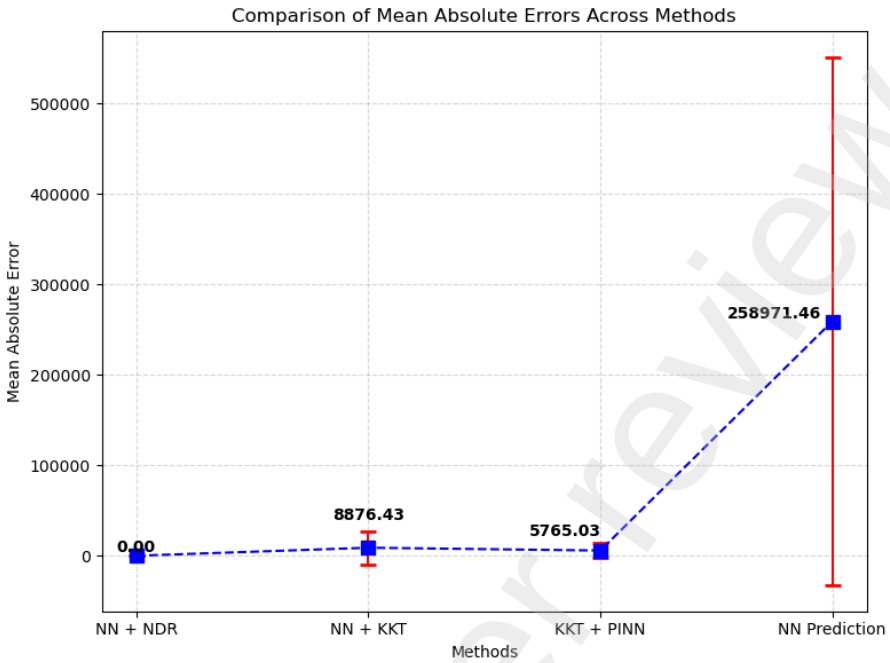


Figure 5 Means absolute error across the different methods

The results, as depicted in Figure 5, show that the KKT × PINN method achieves a significant improvement in accuracy compared to both the standalone NN and KKT × NN approaches. Specifically, the mean absolute error for KKT × PINN predictions is considerably lower than that of KKT × NN. The significant improvement over NN × KKT can be attributed to the complementary effects of the two mechanisms in KKT × PINN: the custom constraint layer of KKT ensures that the

model learns to respect the constraints during training, while the residual term in the loss function reinforces this adherence by penalizing deviations from the equilibrium constant throughout the optimization process. This dual-layer enforcement ensures that the predictions are more consistent with physical laws, leading to greater accuracy.

However, despite its advantages, the KKT × PINN method does not outperform the NN × NDR framework. While the KKT × PINN effectively integrates constraints into the learning process, it is inherently limited by the trade-offs in its loss-function design. Specifically, the model must balance minimizing data-driven errors

with adhering to physical constraints. This balancing act introduces minor residual errors that prevent it from achieving the level of precision attained by the NN × NDR method.

In contrast, the NN × NDR framework bypasses these limitations by separating the prediction and reconciliation processes. The neural network provides an initial estimate based solely on data, and the subsequent nonlinear data reconciliation step directly enforces physical constraints with mathematical rigor, achieving perfect alignment with the desired values. As a result, the NN × NDR approach remains the most precise and reliable methodology.

To conclude, among the four methods analyzed, standalone NN exhibits the highest error due to its lack of constraint enforcement. NN × KKT improves accuracy by introducing a custom constraint correction layer but is limited by minor residual errors. KKT × PINN further enhances performance through dual application of constraints, via the KKT layer and the loss function, outperforming NN × KKT and NN alone. However, NN × NDR achieves unparalleled precision, as its two-step process of prediction and reconciliation rigorously enforces physical constraints, eliminating errors entirely. This highlights NN × NDR as the most robust and accurate approach for integrating data-driven models with physical laws.

5. Testing Robustness to Noise and Data Scarcity

In this section, we assess the performance of our proposed NN x NDR method through two key tests: noisy data testing and data scarcity testing. These evaluations aim to examine the model's effectiveness and resilience when confronted with under noisy conditions and with limited data, providing insights into its stability, adaptability, and overall effectiveness in real-world applications.

5.1. Evaluating Model Performance with Noise Introduction

Testing the robustness of our approach with noisy data is essential as real-world datasets, especially in chemical processes, often suffer from measurement inaccuracies, sensor noise, and other environmental factors. The ability of a model to maintain accuracy and reliability in such conditions is crucial for its practical application. In this context, Gaussian

noise was selected to simulate realistic measurement errors for this study as it is a widely recognized and commonly observed noise distribution technique in measurement systems, especially for continuous variables like in our case that are the flowrates of chemical components. The Gaussian noise was introduced using the equation $y_{noisy} = y_{original} + N(0,\sigma^2)$, where σ represents the standard deviation proportional to the variability inherent in the data, effectively mimics these random errors. This allows us to assess how well our model adapts to and recovers from

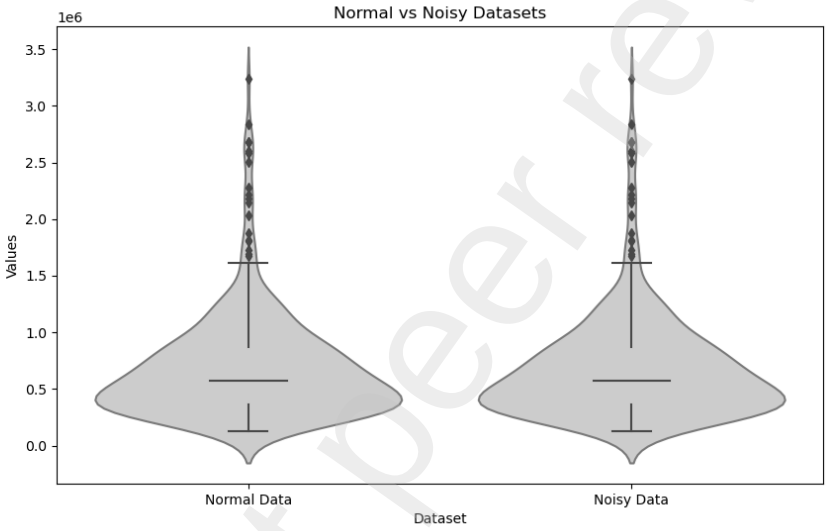


Figure 6 A violin plot that visualizes the similarity of distribution of the output between normal and noisy data.

common data imperfections. However, as we standardize the data prior introducing them to the network, we ensure that the noise becomes relative to the transformed data distribution and that the model is exposed to variability but in a controlled, normalized way.

The results from this testing demonstrated that, despite the presence of noise in the data set introduced to the neural network, the integration of the network with nonlinear data reconciliation maintained high accuracy in adhering to the physical constraints, effectively minimizing deviation from the true equilibrium values as seen in Figure 6.

This violin plot provides a visual comparison between the distribution of errors in the normal and noisy datasets, illustrating the spread and density of the predictions in each case. The similar shape and range of both

distributions indicate that the model's performance remained stable even under noisy conditions, with no significant deviation in the reconciled predictions. This further confirms the robustness and resilience of the NN x NDR framework in preserving physical consistency despite uncertainties and noise in the input data. The findings reinforce the suitability of this methodology for real-world applications where measurement uncertainties and noise are unavoidable.

5.2. Evaluating Model Performance with Sparse Data Inputs

In addition to evaluating the methodology under noisy conditions, we conducted tests to simulate scenarios with limited data availability. Input data to the network (with the previously defined consistent architecture) was deliberately reduced by up to 90%, mimicking real-world constraints where obtaining extensive datasets may be infeasible or resource-intensive. This reduction allowed us to assess the method's ability to maintain reliability and stability in enforcing physical constraints, such as adherence to equilibrium constant conditions, under data-sparse conditions.

Despite the substantial reduction in available data, the proposed NN x NDR methodology demonstrated remarkable robustness, retaining its effectiveness in upholding the physical constraints. The results indicated that even with a 90% decrease in input data, the method was able to maintain accurate constraint enforcement, reinforcing its adaptability and suitability for applications where data scarcity is a limiting factor. Notably, this evaluation yielded patterns similar to those observed in the noisy data testing, with the model's ability to maintain equilibrium conditions remaining consistent.

However, the flowrate predictions for the chemical components made by the neural network were understandably impacted by the data reduction. This variability in predictions, driven by the reduced data input, may be of particular interest to users in scenarios where certain conditions or constraints are more sensitive to input accuracy, therefore it is significant to see this variation. Thus, we focused on one representative chemical component, biphenyl. This choice was made as all components exhibited similar trends, allowing us to isolate and

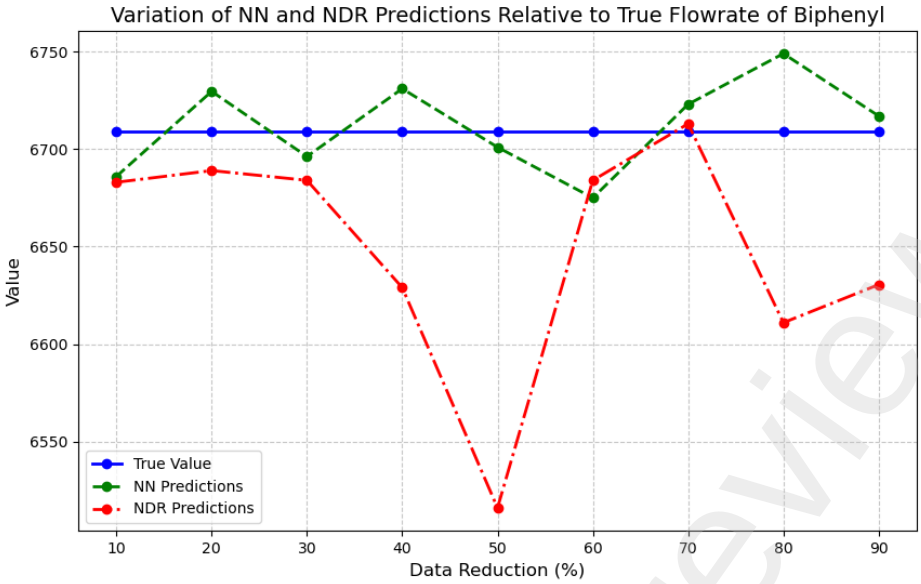


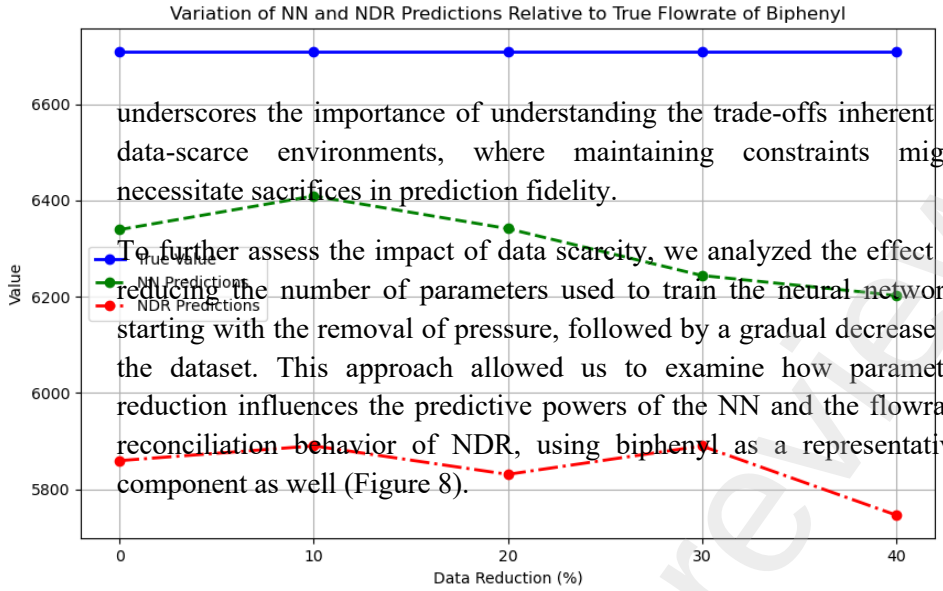
Figure 7 Variation in NN and NDR Performance Under Reduced Data

constraints under reduced data availability.

The NDR framework must adjust the flowrates of components to satisfy the equilibrium constant constraint, even as input data becomes increasingly sparse. This dual effect was assessed in Figure 7 by examining both the predictive accuracy of the NN and the adaptability of the NDR in reconciling the flowrates.

NN predictions displayed a nuanced response to data reduction. At moderate reductions (10%-30%), predictive performance improved, likely due to reduced noise or a decrease in overfitting effects. However, as data availability dropped further, the NN struggled to generalize effectively, resulting in oscillations and significant deviations from the true flowrate values.

NDR's ability to enforce the equilibrium constant constraint was notably sensitive to data scarcity. While it performed reasonably well with moderate reductions, its accuracy began to deteriorate significantly beyond 50% data reduction. This decline may stem from the loss of critical information required to reconcile the flowrates within the physical constraints, causing deviations in the reconciled values while still maintaining the physical constraint satisfied. This interplay



underscores the importance of understanding the trade-offs inherent in data-scarce environments, where maintaining constraints might necessitate sacrifices in prediction fidelity.

To further assess the impact of data scarcity, we analyzed the effect of reducing the number of parameters used to train the neural network, starting with the removal of pressure, followed by a gradual decrease in the dataset. This approach allowed us to examine how parameter reduction influences the predictive powers of the NN and the flowrate reconciliation behavior of NDR, using biphenyl as a representative component as well (Figure 8).

Figure 8 Combined Effect of Parameter Reduction and Data Scarcity on Flowrate Prediction and Reconciliation

Compared to the results from data reduction alone, decreasing the number of training parameters first led to predictions with reduced oscillations. This indicates that parameter reduction may mitigate overfitting effects, forcing the NN to generalize better when fewer inputs are available. Consequently, the combination of fewer parameters followed by data scarcity altered the behavior of the NN, resulting in smoother predictions and better stability across the tested reductions. This phenomenon can be attributed to the removal of redundant or less critical features (such as pressure), which likely constrained the model to focus on the most relevant input features. However, as the data continued to decrease, the NN predictions ultimately began to degrade, exhibiting

deviations from the true flowrate values due to the compounded effect of fewer parameters and sparse data.

NDR followed a trend similar to that of the NN predictions. As its primary objective is to reconcile the flowrates in a manner that adheres to the equilibrium constant constraint, its behavior is inherently tied to the NN predictions, which serve as its input. Thus, the reconciliation process mirrored the NN's trend, showing improved stability during moderate reductions but eventually diverging at higher levels of data scarcity. Despite the overall degradation at extreme data reductions, NDR consistently preserved the physical constraints of the system as we earlier mentioned. This observation highlights its robust capacity to enforce equilibrium constant adherence, albeit with potential sacrifices in prediction accuracy as input data becomes increasingly sparse.

In summary, the analysis under noisy and data-scarce conditions highlights the resilience and robustness of our methodology in enforcing physical constraints, even as predictive accuracy diminishes with increasing input variability or reduction. While the neural network's predictive power is sensitive to data quality and availability, the nonlinear data reconciliation remains steadfast in preserving equilibrium constraints. Ultimately, the balance between predictive precision and constraint enforcement is user-specific as it depends on the particular application and operational needs.

6. Full Process Examination: Reactor-Distillation Integration

The methodology's robustness and applicability were tested using a connected process comprising a Gibbs reactor, a separator, a heat exchanger, and a distillation column (Figure 9). For simplicity in evaluating the method, we focused on the direct connection between the reactor and the distillation column, as the intermediate equipment mainly serves technical purposes and does not present significant challenges in testing the constraint-enforcement capabilities of the methodology. This simplification allowed for a clear examination of how the method performs in enforcing physical constraints across key components of the process.

The analysis began with applying NDR to the reactor's output flowrates predicted by the NN as done previously (1,210 data pts) to enforce the equilibrium constant constraint. By doing so, the reactor's reconciled outputs were aligned with thermodynamic equilibrium, ensuring that the data provided to the distillation column model was consistent with physical principles (Figure 10). For the sake of consistency, the reconciled flow rates exiting the reactor were then fed into a process simulation model developed in ProSim that generates the predicted outputs for the distillation column, which are then used to train and test a neural network (NN) designed to predict the distillation column's behavior.

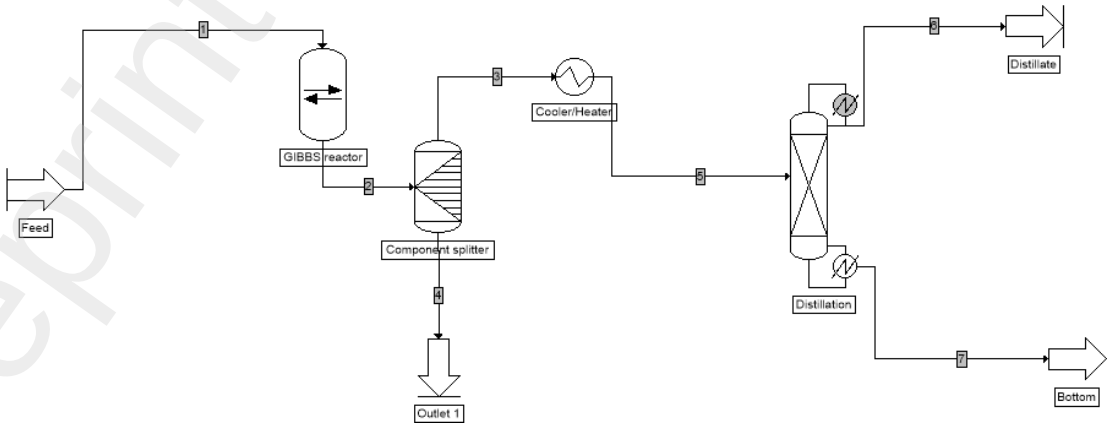


Figure 9 Full process diagram

The column's NN received inputs including reconciled reactor outputs, distillate and reflux flowrates, and efficiency, and it was tasked with predicting the top and bottom flowrates of toluene and biphenyl while keeping an eye on the mass balance as the physical constraint. However, post the NDR reactor's step, only 242 data points were available for the column (using an 80:20 training-to-testing ratio, leaving just 49 points in the test set). This substantial reduction in data caused the NN's predictive performance to weaken, and the flow rate predictions for the top and bottom products became scattered, reflecting the network's struggle with the smaller dataset.

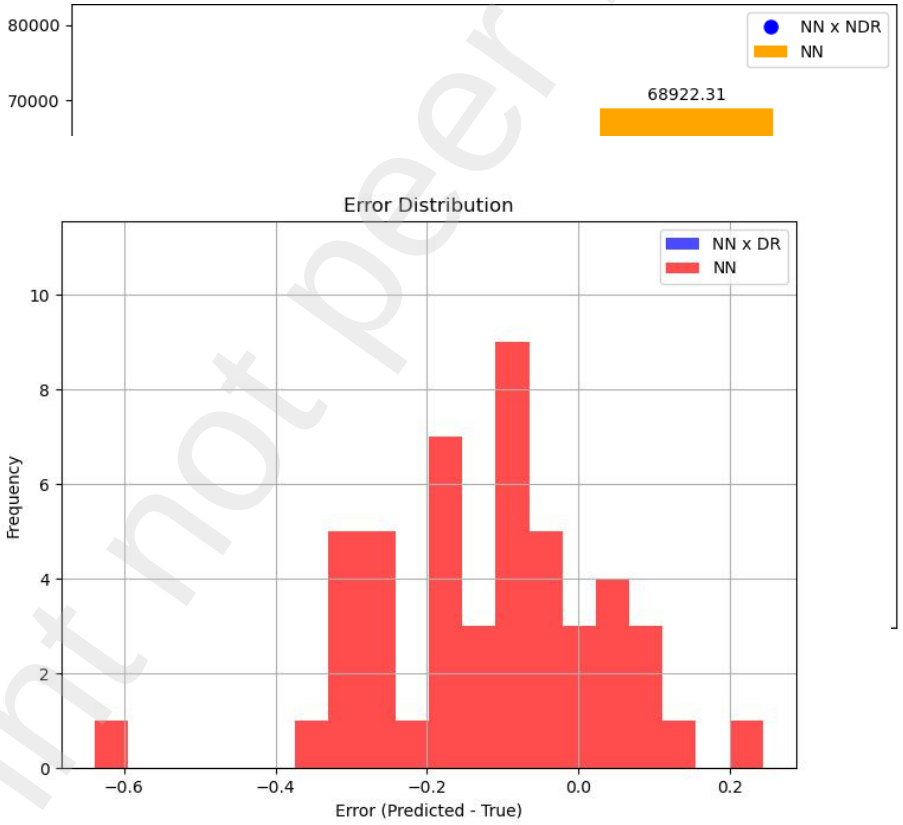


Figure 11 Error distribution of mass balance equality of NN vs NNxDR

To address this challenge, Linear Data Reconciliation (DR) was applied to the NN's predicted flow rates to enforce mass balance. While DR

successfully imposed the mass balance constraint, the reconciled flow rates remained somewhat inaccurate because they were influenced by the NN's initial predictions, which were compromised by the reduced data. The application of DR was effective in enforcing the mass balance achieving full constraint imposition where it achieved zero error distribution compared to a standalone NN (Figure 11), but it did not significantly improve the accuracy of the flow rate predictions as its ability to do so depends on the quality of the initial predictions provided by the network.

The observed deviation in the predictions could be considered either significant or negligible, depending on the user's goals. If the goal is simply to enforce the constraints, the effect of reduced data and its impact on the NN's predictions might be deemed minimal. However, if high predictive accuracy is required in addition to constraint enforcement, the quality of the initial NN predictions becomes paramount. This indicates that robust NN performance that is data-dependent is crucial for the success of this methodology, as the effectiveness of data reconciliation is closely tied to the reliability of the initial NN outputs.

In conclusion, this evaluation underscores the importance of combining neural networks with constraint enforcement techniques in process systems. The method demonstrated the ability to enforce physical constraints, such as the equilibrium constant in the reactor and mass balance in the distillation column. However, its effectiveness depends on the quality of the initial NN predictions. In complex, interconnected systems, where multiple constraints must be enforced, the computational cost may increase due to the need for detailed simulations and reconciliations at each stage. Despite these challenges, the method shows potential for ensuring physical consistency in large-scale systems, as long as NN performance is optimized and sufficient data is available for training and testing.

7. Conclusion

This study presents a hybrid methodology that integrates neural networks (NN) with nonlinear data reconciliation (NDR) to address the dual challenges of predictive accuracy and physical consistency

in chemical process modeling. By combining data-driven insights with robust constraint enforcement, the proposed NN x NDR framework demonstrated its capacity to effectively impose physical laws, such as equilibrium constants and mass balance, across interconnected units while maintaining high predictive fidelity.
The application of this method to reactor-distillation integration revealed its strengths and limitations. In the reactor, NDR successfully reconciled outputs to thermodynamic equilibrium, providing reliable inputs for subsequent modeling stages. In the distillation column, while NDR ensured mass balance, its effectiveness was constrained by the predictive accuracy of the NN, which was notably affected by reduced data availability. These findings emphasize the critical interplay between the quality of NN predictions and the efficacy of reconciliation techniques, underscoring the importance of robust training data for complex, multi-unit systems.

The need for detailed simulations, reconciliations, and iterative optimization across interconnected units might pose challenges, particularly for industrial-scale processes. However, the ability of NN x NDR to ensure physical fidelity while leveraging data-driven efficiency positions it as a promising tool for advancing process systems engineering.

In a nutshell, the method's modular nature allows for flexibility in application, making it adaptable to different systems requiring constraint enforcement. A key strength of this approach is its ability to handle nonlinear constraints explicitly, reducing the likelihood of physically inconsistent predictions. However, like any reconciliation-based method, its performance is influenced by the quality of the initial predictions, meaning that poor neural network training can limit the accuracy of the final reconciled outputs. Additionally, even though the method does offer scalability and adaptability but as system complexity increases, the computational cost of iterative reconciliation may become a consideration for large-scale implementations.

Ultimately, this work highlights the transformative potential of hybrid modeling approaches that bridge empirical insights with first-

principles rigor. By achieving a balance between predictive accuracy and constraint enforcement, the proposed methodology represents a significant step toward reliable, scalable solutions for modern process design and optimization. Future work on the NN x NDR framework could explore its application to a broader range of chemical and industrial processes, particularly those involving dynamic or time-dependent behaviors. Further studies could also assess the method's effectiveness in handling large-scale systems, ensuring its adaptability to more complex process environments, as well. Additionally, the method's efficacy could be investigated in an approach outside the scope of the process's physical behavior and more towards its economic aspect so it would be used to assess not only physical feasibility, but also cost-effectiveness, resource efficiency, and process profitability. Such an extension would make the methodology more valuable for process design, optimization, and decision-making, particularly in industrial settings where balancing technical performance with financial viability is critical.

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