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Research Article

Improved Conversion Performance in Methyl Chloride Production from Methanol and Hydrogen Chloride Through Heat Exchanger Based Waste Heat Recovery and Process Modification

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Abstract

Methyl chloride (CH_3Cl) is an essential intermediate in the manufacture of silicones, agrochemicals, amines, refrigerants, and synthetic rubber; however, conventional production routes are constrained by substantial energy inefficiencies and exergy destruction. This study seeks to enhance the hydrochlorination of methanol to methyl chloride by integrating heat exchangers (HE) as a waste-heat recovery strategy. Simulation software was used to simulate both the baseline and heat-integrated process configurations, employing the Peng–Robinson EOS to represent thermodynamic behavior. In the baseline system, the process required 12,302.48 kW of energy input and produced 9,028.60 kW of useful output, achieving a conversion of 73.4%, with unrecovered hot streams contributing significantly to entropy generation. The modified configuration introduced three heat exchangers (E-100, E-101, E-102) to recover reaction and condensation heat, enabling feed preheating and reducing external utility demand. This integration increased conversion from 73.4% to 95%, raised energy output to 11,912 kW, and reduced both energy losses and exergy destruction. The resulting dataset from the optimized system was subsequently evaluated using machine learning models, among which Bayesian Ridge Regression (BRR) demonstrated the highest accuracy and stability, exhibiting superior MSE, MAE, and R^2 performance. Overall, the findings show that coupling heat-integration strategies with machine-learning analysis provides a robust pathway for improving energy efficiency, product quality, and predictive reliability in methyl chloride production.

Keywords: Methyl Chloride Production; Heat Exchanger Integration; Simulation Software; Improving Conversion

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1. Introduction

Methyl chloride (chloromethane, CH_3Cl) is a colorless, volatile liquid with a characteristic odor that is soluble in water; it has a boiling point near 249 K and a reported density of about 353 g/lt, and is typically handled under atmospheric pressure conditions for storage and operation [1]. The compound is widely used as a feedstock and solvent in industries producing silicones, agricultural chemicals, amines, refrigerants, and butyl rubber, but it is also identified as a carcinogen in inventories of toxic releases [2]. Upstream production of chloromethane involves several reactors and separation stages, with the principal chemical step being the hydrochlorination of methanol.

The reaction in Equation (1) is thermodynamically classified as exothermic, with a negative standard enthalpy change at 298 K. This characteristic strongly impacts the reactor's thermal dynamics and the overall energy balance of the process. Consequently, considerable heat is

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liberated during operation, influencing energy efficiency and contributing to system irreversibility. Therefore, developing a dependable method to calculate energy and exergy balances for industrial chloromethane routes is crucial to manage process complexity and improve day-to-day operational efficiency [3].

Industrial production of methyl chloride can follow multiple routes. One route is the chlorination of methane with chlorine gas at roughly 400 °C and 20 atm, proceeding via:

$$CH_4\ (g) + Cl_2\ (g) \rightarrow CH_3Cl\ (g) + HCl\ (g) \quad (1)$$

Thermodynamically, the reaction exhibits an exothermic heat effect under standard conditions (298 K). However, in industrial practice, elevated operating temperatures are necessary to attain high conversion levels. This reaction with reported methane conversion around 90% and final product purity near 99% [4]. Another common route is the catalytic reaction of methanol with hydrogen chloride: equimolar vapors of methanol and HCl are vaporized and fed to a fixed-bed multitube reactor operated at about 340–350 °C and 1.3 atm, using a 2 mm alumina gel catalyst; this route can achieve roughly 95% conversion of methanol, after which vapor-phase streams are recycled and liquid fractions are sent to distillation to yield chloromethane at about 99.5% purity, with residual methanol and water as byproducts [5].

The basic production process of methyl chloride via the hydrochlorination pathway continues to face significant challenges in energy efficiency. The system tends to release the exothermic reaction heat directly into the environment without further utilization, thereby contributing to both energy and exergy losses throughout the process. This result aligns with previous research showing that traditional process designs experience substantial exergy destruction, especially in the reactor section, because of uneven heat distribution and the lack of internal heat-recovery systems [2]. In the baseline process used as the reference for this study, similar phenomena are evident in several hot streams such as reactor effluent, medium temperature recycle flows, and condensation heat from separation stages that are not recovered and are instead discharged entirely through cooling utilities. The inability of the system to manage and integrate internal heat represents a critical factor that reduces overall energy efficiency and potentially hinders reaction performance. These conditions underscore the necessity of optimization efforts through heat integration strategies, enabling the process to operate with greater thermodynamic efficiency, while minimizing energy losses inherent in the baseline configuration.

The incorporation of a heat exchanger (HE) as a waste heat recovery strategy represents a highly relevant approach to enhancing the exergy efficiency of process systems. Heat pipe heat exchangers have been widely implemented across various industries as an effective technology for waste heat recovery, owing to their ability to transfer heat efficiently without requiring additional pumps or external energy, thereby significantly improving overall system performance [6]. In addition, previous studies have shown that incorporating waste heat recovery technologies into integrated energy systems can significantly lower primary energy use and dependence on external utilities, while also improving overall exergy efficiency [7]. Such advancements are particularly critical in the broader context of transitioning toward sustainable energy systems.

The objective of this study is to develop a comprehensive framework for improving the energy and exergy efficiency of industrial methyl chloride production, with a particular focus on the hydrochlorination of methanol route. Specifically, the research aims to identify critical sources of energy loss and exergy destruction in the baseline process—such as unrecovered reactor effluents, recycle streams, and condensation heat—and to address these inefficiencies through the integration of heat exchangers as waste heat recovery units. By incorporating heat integration strategies into the process design, the study seeks to enhance conversion performance, reduce reliance on external utilities, and minimize irreversibility, thereby advancing the thermodynamic sustainability of methyl chloride production. Furthermore, the study explores the application of machine learning models to validate and predict system behavior under both baseline and modified configurations, establishing a robust methodology that combines process simulation and data-driven approaches to optimize energy utilization, improve product quality, and support the transition toward more sustainable chemical manufacturing practices.

2. Methods

2.1 Basic Process Simulation

The baseline process simulation in this study was conducted using Aspen HYSYS V11, employed as a modelling platform to represent the thermodynamic behaviour, reaction kinetics, and mass energy balances of the methyl chloride production system. The thermodynamic framework was developed using the Peng–Robinson Equation of State (EOS) property package, selected for its proven reliability in predicting phase equilibria of hydrocarbon mixtures and volatile polar components that dominate the hydrochlorination reaction. This selection aligns with previous methodological approaches that highlight the importance of precise thermodynamic modeling for reliable experimental assessment and exergy analysis [2].

The operating parameters of the baseline process were established to reflect conventional hydrochlorination conditions: reactor temperature of 105 °C, pressure of 3 bar, and feed rates of methanol and hydrogen chloride of 16,255.6 kg/h and 11,423.9 kg/h, respectively. These parameters were selected to represent a typical industrial configuration, thereby allowing the simulation results to serve as a benchmark for assessing energy efficiency and identifying opportunities for process optimization.

Energy performance was evaluated through two principal indicators: Energy Loss (Q_{loss}) and Exergy Destruction (Ex_D). Energy loss was quantified as the difference between total heat input and output, expressed as:

$$Q_{loss} = Q_{in} - Q_{out} \tag{2}$$

This relatively modest efficiency highlights the potential for internal heat recovery to enhance thermal performance.

Exergy destruction was analyzed using the physical exergy formulation [8]:

$$Ex_D = T_0 \Delta S_{gen} \tag{3}$$

where $T_0 = 298\ K$ represents the environmental reference temperature, and ΔS_{gen} denotes entropy generation due to process irreversibility. The observed energy loss of 3,273.88 kW implies significant entropy generation, particularly within the reactor, which is recognized as the dominant contributor to exergy destruction in hydrochlorination systems.

Moreover, the simulation identified several unrecovered hot streams in the baseline configuration including reactor effluent, medium temperature recycles flows, and latent heat from condensation stages that were discharged entirely through cooling utilities. The absence of internal heat recovery mechanisms in these streams exacerbates energy loss and entropy generation, confirming that the baseline configuration remains thermodynamically suboptimal. These findings underscore the necessity of implementing heat integration strategies to improve overall energy efficiency and reduce irreversibility within the methyl chloride production process.

2.2. Creating a New Dataset

Model modified with the addition of a heat exchanger (HE) represents a crucial step in evaluating thermodynamic systems. Sensitivity analysis enables the identification of input variables that exert the greatest influence on system outputs. This approach is considered particularly valuable for analyzing how complex systems behave, making the revised dataset more suitable for optimization efforts and the development of data-driven models [9].

Although the input and output variables remain the same, the inclusion of HE introduces differences in the output range. Changes in the heat exchanger network configuration directly affect the thermal profile and system efficiency. IEEE (2022) demonstrated that modifications to HE networks within HYSYS simulations can significantly alter system performance. Therefore, the simulation dataset reflects the updated system conditions and is more suitable for further analysis. To ensure dataset quality, normalization procedures are applied so that machine learning models are not biased by data scale. Proper normalization and appropriate data partitioning are emphasized as key steps for improving a model's predictive accuracy and its ability to generalize effectively to new data [10]. With this approach, the simulation dataset is well-prepared for predictive analysis and process optimization supported by artificial intelligence.

2.3. Model Machine Learning

The development of machine learning models was carried out to predict energy loss and exergy destruction based on simulation datasets generated from Aspen HYSYS. These datasets were constructed from two process configurations: the basic process and the modified process (incorporating heat exchangers). The dataset included four input variables molar feed rate, reactor temperature, energy input, and exergy input which were varied to produce a total of 235 data points. All data were normalized and divided into training and testing sets.

Eight machine learning models were evaluated to determine which was most effective in capturing the relationship between process variables and energy losses. The models were selected to represent diverse methodological approaches: Bayesian Ridge Regression (BRR) and Stochastic Gradient Descent (SGD) as regularized linear regressions; K-Nearest Neighbours Regression (KNR) and Support Vector Regression (SVR) for proximity-based pattern recognition; Artificial Neural Networks (ANN) for modelling complex nonlinear relationships; and ensemble methods such as Random Forest Regression (RFR), Gradient Boosting Regression (GBR), and AdaBoost Regression (ABR), which combine multiple estimators to enhance robustness.

All models were assessed using three evaluation metrics: Mean Squared Error (MSE), Mean Absolute Error (MAE), and R-squared (R^2), defined as [11]:

$$\text{MSE}=\frac{1}{N}\sum_{i=1}^{N}(y_{pr,i}-y_{tr,i})^2 \quad (4)$$

$$R^2 = 1-\frac{\sum_{i=1}^{N}(y_{pr,i}-y_{tr,i})}{\sum_{i=1}^{N}(y_{pr,i}-y_m)} \quad (5)$$

$$\text{MAE}=1-\frac{\sum_{i=1}^{N}(y_i-x_i)}{N} \quad (6)$$

The evaluation results demonstrated that Bayesian Ridge Regression (BRR) achieved the most superior performance. BRR consistently provided stable predictions across both baseline and modified process datasets, yielding the highest R^2 value (≈ 0.998) and the lowest MSE and MAE among all models. This indicates that BRR's predictions closely matched the Aspen HYSYS simulation outputs. Consequently, BRR was selected as the optimal model to validate the impact of heat exchanger modifications on energy efficiency and to estimate energy loss and exergy destruction under varying operating conditions.

3. Results and Discussion

3.1. Basic Process Description and Simulation

Figures 1 and 2 serves as the process reference for this study. The flowchart illustrates the unmodified production scheme of methyl chloride and functions as the starting point for all subsequent calculations and evaluations. For this baseline scheme, the fundamental equations applied to perform the mass balance, thermal energy balance, and exergy balance are:

$$m_{in} = m_{out} \quad (7)$$

$$E_{in} - E_{out} + Q_{in} - Work_{out} = E_1 \quad (8)$$

$$Ex_{in} - Ex_{out} + Ex_{heat} - Ex_{work} = I_d \quad (9)$$

Simulation results revealed that the system received an energy input (Q_{in}) of 12,302.48 kW, while the energy output (Q_{out}) was 9,028.60 kW, yielding an energy loss of Q_{loss}=3,273.88 kW. This corresponds to approximately 26.6% of the input energy not contributing to useful process work. The overall energy efficiency (η) of the baseline system was calculated as:

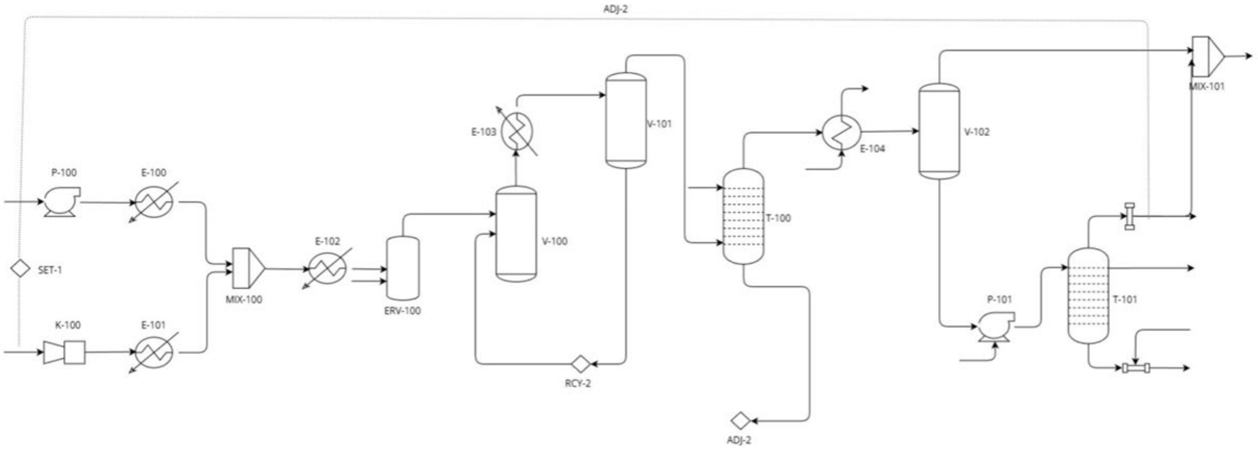

Figure 1. Process flow diagram (PFD) of basic (unmodified) process of methyl chloride production [2].

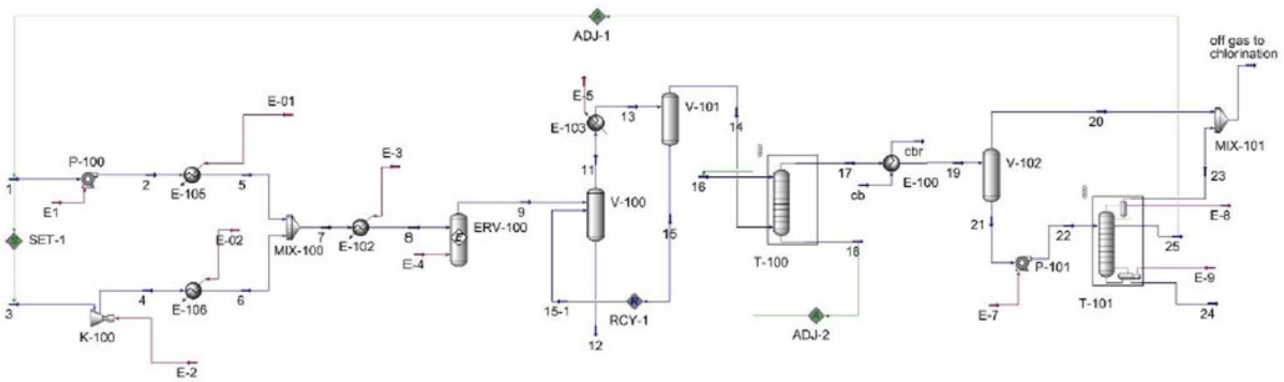

Figure 2. Process simulation of basic (unmodified) process of methyl chloride production using Aspen HYSYS.

$$\eta = Q_{out} / Q_{in} \times 100\% = 72.36\% \quad (10)$$

The results derived from the baseline process establish the performance benchmarks. Specifically, the data indicate a conversion of 72.36% with an energy input of 12,302.48 kW. This benchmark sets the minimum performance target that the optimized model must successfully exceed.

Figures 3 and 4 presents the modified process flow diagram, which represents mass and energy balances, raw thermodynamic data, and kinetic datasets. The overall approach combines soft computing models with HYSYS simulation to bridge research gaps and predict process performance with greater accuracy. The specific objectives of the modelling effort were: (1) to develop a HYSYS model capable of generating a comprehensive methyl chloride plant dataset; (2) to assess the HYSYS model's competency and produce finalized datasets via hyperparameter tuning; (3) to validate and train the simulation dataset using supervised data science methods ; and (4) to compare all candidate models to identify the best performer for developing an HYSYS-based predictive tool.

The comparison in Table 1 highlights the effectiveness of the HYSYS–ML framework in optimizing the process represented by Figure 4. The reference data (from Figure 1) records a conversion of 72.36% with an energy input of 12,302.48 kW. In contrast, the modified data (from the Figure 4 model) achieves a substantially higher conversion of 95%, although the total energy input increases to 15,374 kW and the energy output reaches 11,912 kW. The observed 22.6% increase in conversion required an additional energy input of approximately 3,071 kW. This supplementary energy is necessary because maintaining higher operating conditions is essential for achieving optimal reaction rates. Although the hydrochlorination reaction is exothermic, maximizing the yield (95%) within the defined reactor residence time requires a significant increase in the reaction rate constant (k). From a kinetic perspective, raising the temperature is critical, as dictated by the Arrhenius relation:

$$k = A.\exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

This fundamental equation explains that the rate constant (k) increases exponentially with the absolute temperature (T). The additional energy input is therefore strategically utilized to sustain

Table 1. Process flow diagram (PFD) for modified methyl chloride production process.

Parameter Type	References Data	Modification Data
Input (Energy Input (kW))	12,302.48	15,374
Output (Energy Output (kW))	9,028.60	11,912
Result of Methyl Chloride Conversion	72.36%	95%

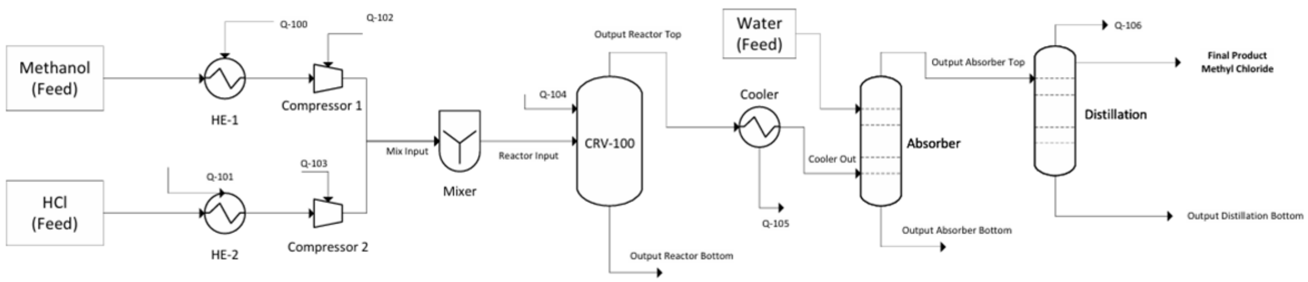

Figure 3. Process flow diagram (PFD) for modified methyl chloride production process.

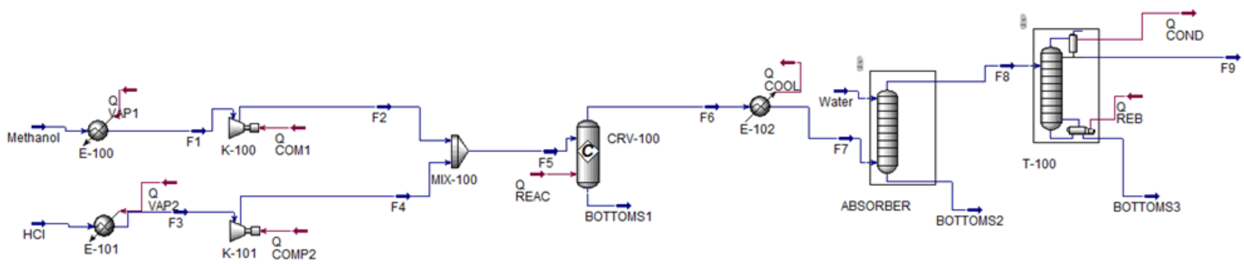

Figure 4. Process simulation of the modified methyl chloride production process using Aspen HYSYS.

the necessary higher operating temperature, ensuring that k increases sufficiently so that the desired conversion (yield) of 95% can be achieved within the same residence time [12].

3.2. Performance of ML Models on Modified Processes

The process flow diagram (PFD) represents the synthesis and purification of methyl chloride via the reaction of methanol with hydrochloric acid. The diagram outlines the main stages of the process, beginning with the preparation and mixing of feed streams, followed by the chemical reaction in the reactor, and continuing with cooling, absorption, and distillation for product separation. Each unit operation such as mixers, compressors, heat exchangers, absorber, and distillation column is arranged to ensure that the reaction proceeds under controlled thermal conditions and that the desired product is efficiently recovered while by-products and excess reactants are removed [13]. This configuration highlights both the chemical transformation and the energy integration strategy applied to optimize utility consumption.

Heat exchanger E-100 is positioned upstream of the reactor and functions to preheat the feed (F1/F2) before entering CRV-100. In a heat integration configuration, E-100 receives energy from hotter process streams, thereby acting as a heat recovery unit and reducing the demand for external heating such as steam. Meanwhile, E-101 is located on the reactor effluent line (F5) and serves to cool the effluent before separation. The sensible heat removed by E-101 can be utilized to preheat the feed via E-100 or transferred to other streams requiring energy, thus lowering the load on external cooling utilities. E-102 is placed in the distillation column condensation section (associated with overhead streams such as F9/BOTTOMS2) and functions to condense vapor. Since it handles condensation, E-102 enables significant recovery of latent heat and, when applied for preheating, can reduce the load on the refrigeration system, including compressors K-100/K-101 [14].

In designing the heat exchangers, several assumptions are applied, including the Minimum Approach Temperature ($\Delta T_{\min}$), which defines the minimum temperature difference between hot and cold streams, conservative fouling factors for streams containing HCl, and average heat transfer coefficients according to the phases involved. A small $\Delta T_{\min}$ increases heat recovery and reduces external utility demand but requires larger exchanger areas and higher capital costs. Conversely, a larger $\Delta T_{\min}$ reduces equipment size and cost but increases steam and cooling utility consumption [15]. Due to the presence of HCl, selecting corrosion-resistant materials and applying conservative fouling factors are essential to ensure reliable operation.

The addition of heat exchangers directly alters utility loads by transferring energy from hot process streams to cold streams. External heater and cooler requirements are reduced, and quantitatively, the utility savings are approximately equal to the energy recovered minus losses due to fouling and thermal limits. In practice, this reduces QREB and QCOND in the distillation column and decreases compressor work in the refrigeration system if E-102 lowers the condenser load. Based on the compositions and annotations in the PFD, reaction heat from the reactor effluent (F5) represents a potential internal energy source that can be recovered via E-101 or E-102 to preheat the feed through E-100, thereby reducing steam demand and lowering external cooling loads. In accordance with previous studies, improving energy efficiency in this process is achieved by applying heat-integration strategies, where heat exchangers recover thermal energy from product streams to preheat the reactor feed [16]. This statement reinforces the practice evident in the PFD, namely the use of product or effluent heat for feed preheating.

The performance of machine learning (ML) models in the modified process was evaluated using a new dataset generated from Aspen HYSYS simulations after the integration of heat exchangers (HE). The modified dataset exhibited lower and more stable distributions of energy loss and exergy destruction, reflecting the improved efficiency of internal heat utilization. Overall, all models demonstrated enhanced predictive accuracy when applied to the modified dataset, although the relative performance differences among models remained consistent with the trends observed in the baseline process.

Revalidation results confirmed that Bayesian Ridge Regression (BRR) continued to be the best-performing model in the modified system. BRR achieved the lowest MSE and MAE values compared to other models, indicating that the Bayesian regression approach was able to maintain stable performance even as data characteristics shifted due to improved process efficiency. The ability of BRR to adapt to data patterns and preserve predictive stability highlights its strong parameter sensitivity and its capability to track changes in energy distribution within the modified process configuration.

Residual analysis further reinforced these findings. The residual plots of BRR revealed errors that were random, symmetric, and centered around zero, with no discernible bias or systematic deviation. The tighter residual distribution in the modified dataset also indicated that a more efficient system produces more consistent data and enables more precise predictions. Accordingly, BRR is identified as the most accurate and stable model for evaluating thermodynamic performance in methyl chloride production processes that have undergone energy efficiency improvements through heat exchanger integration.

3.3. Significance

The modification of the system through the integration of a heat exchanger (HE) produces more accurate simulation data for training machine learning (ML) models. Such enhanced datasets enable the development of predictive maintenance systems capable of identifying potential failures before they occur. Previous studies have demonstrated that ML models trained using real-time thermodynamic data can significantly improve the operational reliability of industrial processes [17]. With higher predictive accuracy, maintenance activities can be scheduled in a timely and efficient manner, thereby reducing unexpected disruptions.

The integration of ML models with the modified thermal system also contributes directly to lowering operational costs. Evidence shows that AI-driven predictive maintenance can substantially reduce equipment downtime and decrease overall energy consumption [18]. In parallel, waste heat recovery through HE reduces reliance on external utilities, thereby lowering energy expenditures. The combination of improved thermal efficiency and intelligent maintenance establishes a system that is both cost-effective and sustainable.

This strategy reflects a major trend in modern process industries. Reports indicate that predictive maintenance enhanced by ML and IoT-based sensing technologies can boost operational efficiency and extend equipment lifespan [19]. Supported by accurate simulation data, maintenance systems become more adaptive to real operating conditions. The practical implication of this modification is the creation of an industrial ecosystem that is more resilient, efficient, and increasingly driven by smart technologies.

4. Conclusions

This study achieved its objective of improving the energy and exergy efficiency of methyl chloride production via the hydrochlorination of methanol by modifying the baseline process with integrated heat exchangers. The incorporation of heat recovery units successfully addressed major sources of energy loss and exergy destruction, enabling the reutilization of reactor effluent and condensation heat that were previously discharged. As a result, the modified configuration enhanced conversion performance from 72.36% to 95%, increased energy output, and reduced reliance on external utilities, thereby minimizing irreversibility and strengthening overall thermodynamic sustainability. In addition, the application of machine learning models, particularly Bayesian Ridge Regression, provided accurate and stable predictions of energy loss and exergy destruction, validating the effectiveness of the modified system. These outcomes confirm that heat integration combined with predictive modeling offers a reliable pathway to optimize energy utilization, improve product quality, and support the transition toward more sustainable chemical manufacturing practices.

CRedit Author Statement

Author Contributions: Fadhillah Ghania Putri: Supervision, Writing – Review & Editing, Software, Writing - Original Draft (Conclusion), Validation; Nurfi Misyka: Conceptualization, Methodology, Software, Data Curation, Writing - Original Draft (Abstract), Visualization; Viviana Kumala Dewi: Methodology, Formal Analysis, Investigation, Writing – Original Draft, Formal Analysis, Writing, Visualization; Farsya Mutiara Kansha: Investigation, Formal Analysis, Validation; Aisya Salsabila Khairani: Resources, Data Curation, Investigation, Formal Analysis, Writing. All authors have read and agreed to the published version of the manuscript.

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