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Simulation and Economic Evaluation of Methylene Chloride Production via Methane Chlorination

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ABSTRACT

This study simulates and economically evaluates methylene chloride production via methane chlorination using Aspen HYSYS V11. A plug flow reactor (PFR) model optimized reaction conditions to 280°C and 2 bar with a methane-to-chlorine ratio of 1.5, achieving 51.68% methane conversion and 99% methylene chloride purity. Sensitivity analysis confirmed these parameters maximize yield while minimizing by-products (methyl chloride, chloroform, carbon tetrachloride). Sustainable design principles guided process integration, including sodium hydroxide/water absorption for HCl neutralization and distillation columns for product separation. By-product recovery enhanced profitability, yielding 97%-purity methyl chloride. Economic feasibility was assessed via Total Annual Cost (TAC) methodology, combining capital and operating expenditures. For a 1700 ton per year capacity, the TAC was $297000 per year, with by-product credits significantly improving economic viability. The design reduced energy consumption and waste through heat integration and efficient separation. This work demonstrates a scalable, economically resilient methylene chloride production process, highlighting the synergy between operational optimization, sustainable engineering, and profitability in industrial chlorination systems.

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1. Introduction

Methylene chloride serves as a crucial intermediate in the synthesis of various industrially significant chemicals. Its widespread applications are driving a steady increase in global market demand. To meet this demand, numerous companies are either expanding their existing production capacities or constructing new facilities. However, due to methyl chloride's highly flammable, toxic, and potentially carcinogenic properties, stringent environmental regulations have led to a moderate growth rate in di-chloromethane production [1-3].

Currently, two main industrial methods are employed for di-chloromethane production: methane chlorination and the hydrochlorination of methanol [1, 4]. The direct chlorination of methane is beneficial for achieving high yields while minimizing by-products [5]. Although laboratory-scale investigations have aimed to optimize chloromethane conversions, particularly using molecular chlorine in conjunction with oxy-hydrochlorination catalysts, scaling these methods to industrial levels has faced significant practical challenges. Temperature is a critical factor influencing conversion rates in methane chlorination, which can also lead to the formation of other chloromethanes such as methyl chloride, chloroform, and carbon tetrachloride. This method is particularly advantageous when the production of higher chloromethanes is desired [5, 6]. However, due to the existing issues with scaling laboratory processes, industries continue to rely on the current two production routes. Therefore, this research is focused on innovating ways to improve the efficiency of existing industrial processes.

To boost production rates, the industry must tackle various challenges inherent in process design and operation. Low operational efficiency, energy wastage, difficulties in process control, issues with emission estimation, inadequate product storage knowledge, and underpricing of safety equipment are just a few of the hurdles encountered by process industries [7, 8]. Research indicates that these challenges can be effectively addressed through the implementation of sustainable design methodologies in the early stages of process design using process systems engineering. This approach can decrease the time required for the conceptualization and design of new or improved process facilities while ensuring that they operate safely and with minimal environmental impact over their anticipated 30–50-year lifespan [7, 9].

The existing literature clearly indicates that plant design significantly influences energy consumption, capital expenditure, and safety. Incidents related to safety can lead to substantial operational losses, damage, and revenue decline, with long-lasting repercussions for both workers and the community [10].

Recent studies demonstrate significant efforts to optimize methane chlorination processes using Aspen HYSYS. Yandrapu and Kanidarapu (2021) [5] developed a comprehensive simulation model for methyl chloride production via methane chlorination, emphasizing operational parameter optimization (temperature, pressure, reactant ratios) and process safety. Their HYSYS-based study established that reactor temperatures of 350–400°C and a CH_4:Cl_2 molar ratio of 1.5 maximize methyl chloride yield while accurately predicting industrial-scale behavior. Crucially, their work confirmed HYSYS's capability to address scalability challenges inherent in chlorination processes. Similarly, Kim et al. (2022) [8] integrated advanced kinetic models with HYSYS simulations to analyze plug-flow reactor (PFR) dynamics in direct methane chlorination. They validated that precise control of reactor temperature (280–320°C) and pressure (1.5–2 bar) enhances methane conversion to 40–50% while suppressing unwanted by-products (e.g., chloroform, carbon tetrachloride). These studies collectively underscore HYSYS's robustness in simulating reaction kinetics and separation units for industrial chloromethane synthesis.This study introduces several innovative approaches to enhance the efficiency and sustainability of methylene chloride production via methane chlorination. By leveraging advanced simulation techniques using Aspen HYSYS V11, we have developed a robust process model that facilitates the optimization of key operational parameters, specifically reactor temperature, pressure, and reactant ratios. Furthermore, our research emphasizes the strategic integration of by-product recovery mechanisms for methyl chloride, carbon tetrachloride, and chloroform, thereby transforming waste into valuable resources. This not only improves the economic viability of the production process but also aligns with contemporary sustainability goals within the chemical industry. Additionally, our focus on implementing sustainable design methodologies and process systems engineering principles presents a novel framework for addressing common operational challenges, promoting enhanced safety and reduced environmental impact throughout the production lifecycle. Overall, this work contributes significant insights into the advancement of methylene chloride production, supporting the transition toward more efficient and eco-friendly chemical manufacturing practices.

2. Process description and simulation

2.1. Process overview and reaction mechanism

A standard industrial methane chlorination facility designed to produce methylene chloride as the main product is outlined in Fig 1. The simulation model was developed using Aspen HYSYS V11. In this process, a mixed gas stream comprising methane and chlorine is introduced into a furnace (Reactor) equipped with a shell and tube system designed for feed preheating to an optimal inlet temperature of 280°C. The reactor operates at a temperature of 400°C. Reactions present in the process are given in Eqs. (1)-(5). Conversion values for the reaction (2) is 39.98%, reaction (3) is 51.68%, reaction three is 0.4123%, reaction (5) is 4.066×10−4% and for reaction (6) is 98.09%. The reactions along with their kinetic data are given below [6].

$$Cl_2 \longrightarrow 2Cl^- \,(Radical\ generation) \tag{1}$$

$$\begin{gathered} 2CH_4 + Cl_2 \longrightarrow 2CH_3Cl + 2H_2 \\ \begin{pmatrix} CH_4 + Cl^- \longrightarrow CH_3 + HCl \quad (Hydrogen\ abstraction) \\ CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl^- \quad (Chlorination) \end{pmatrix} \\ -r = 1.2\times10^{16}\exp\left(\frac{-1.15\times10^{5}\,\frac{kj}{mol}}{RT}\right) \end{gathered} \tag{2}$$

$$\begin{gathered} 2CH_3Cl + Cl_2 \longrightarrow 2CH_2Cl_2 + H_2 \quad (Methylene\ chloride\ formation) \\ -r = 1.4\times10^{12}\exp\left(\frac{-63000\,\frac{kj}{mol}}{RT}\right) \end{gathered} \tag{3}$$

$$\begin{gathered} 2CH_2Cl_2 + Cl_2 \longrightarrow 2CHCl_3 + H_2 \\ -r = 8.9\times10^{9}\exp\left(\frac{-75000\,\frac{kj}{mol}}{RT}\right) \end{gathered} \tag{4}$$

$$\begin{gathered} 2CHCCl_3 + Cl_2 \longrightarrow 2CCl_4 + H_2 \\ -r = 5.5\times10^{9}\exp\left(\frac{-85000\,\frac{kj}{mol}}{RT}\right) \end{gathered} \tag{5}$$

$H_2 + Cl_2 \longrightarrow 2HCl$

$$-r = 1.5\times10^5 \exp\left(\frac{-120\frac{kj}{mol}}{RT}\right) \tag{6}$$

The methane to chlorine ratio is adjusted to control the desiredproduct distribution. The reactor inlet pressure is increased to 2 bar using a compressor (K-101) and the inlet temperature of the stream is increased to 280°C using a heat exchanger (E-100). The gaseous products are then cooled to 200°C in a heat exchanger (E-100). This cooled mixture is directed to an absorber (T-100), where a mixture of water (96% mol) and sodium hydroxide (4% mol) is used as an absorbent to capture hydrogen chloride (HCl), resulting in the formation of a liquid HCl solution, which is subsequently neutralized. The division of the water stream into two separate streams, which are subsequently introduced at two different equilibrium stages of the T-100 column, is strategically implemented to enhance the interaction between hydrochloric acid (HCl) and the aqueous sodium hydroxide (NaOH) solution. This approach facilitates improved mass transfer and reaction kinetics, thereby maximizing the efficiency of HCl absorption and neutralization. By optimizing the contact surface area and residence time between the reactants, this configuration promotes a more effective neutralization process, ultimately leading to a higher conversion rate and improved operational performance within the absorber column. The following is the kinetics of the reaction carried out in the T-100 column.

$HCl + NaOH \longrightarrow NaCl + H_2O$

$$-r = 900\exp\left(\frac{-20\frac{kj}{mol}}{RT}\right) \tag{7}$$

The stream (MC), which includes unreacted methane and products, is then introduced into a drying column (T-101) where concentrated sulfuric acid is utilized to eliminate moisture. Subsequently, the treated gas mixture is sent to a partial condenser (E-103). The output from the condenser is sent to a phase separator (V-101) for further processing. Column (T-102) separates methyl chloride, a by-product, with a purity of 97%, and the remaining products are transferred to other columns. Column (T-104) separates methylene chloride, the main product of the process, with a purity of 99%, and carbon tetrachloride is separated in the (T-103).

3. Process simulation

The methylene chloride production process via methane chlorination was simulated using the Aspen HYSYS V11 interface. Given that the process involves electrolyte solutions, such as sodium chloride, the NRTL electrolyte fluid package was selected. To ensure accurate representation of the actual process, several adjustments were made during the simulation.

The reactor/furnace configuration includes a jacket for heat exchange between the feed and products to recover energy. In the simulation, a heat exchanger (E-100) heats the feed to 280°C before it enters the reactor (PFR-100). A logical operation, SET, adjusts the flow rate of the chlorine stream to react appropriately with the methane from the feed mixture (FEED-MIX). The chlorine molar flow rate is set to be 0.5556 times that of the feed mixture, resulting in a ratio of CH4 to Cl2 of 1.5. The reactor (PFR-100) is modeled as a plug flow reactor with the relevant equilibrium reactions defined. To manage the exothermic nature of the reaction, a cooling stream (Q-101) is incorporated. The distillation column (T-103), for separating the by-product, contains 20 separation stages, with feed introduced at stage 15; the column experiences a total pressure drop of 10kPa. Columns T-104 and T-105 are dedicated to recovering dichloromethane and chloroform, respectively, each comprising 20 stages and configured for 99% recovery of the main components. The sizing results of the absorption and distillation columns are given in Table 1.

Table 1. The sizing results of the absorption and distillation columns

Column No.	T-100	T-101	T-102	T-103	T-104
Stages	14	10	20	15	20
Feed Stage	-	-	15	10	10
Column height (m)	4.2	3	6.2	6	7.1
Column diameter	0.7589	0.7039	0.95	0.8575	1.1
Operating Temperature (°C)	30	25	60	61	61
Operating Pressure (bar)	1	4	2	1	1.5

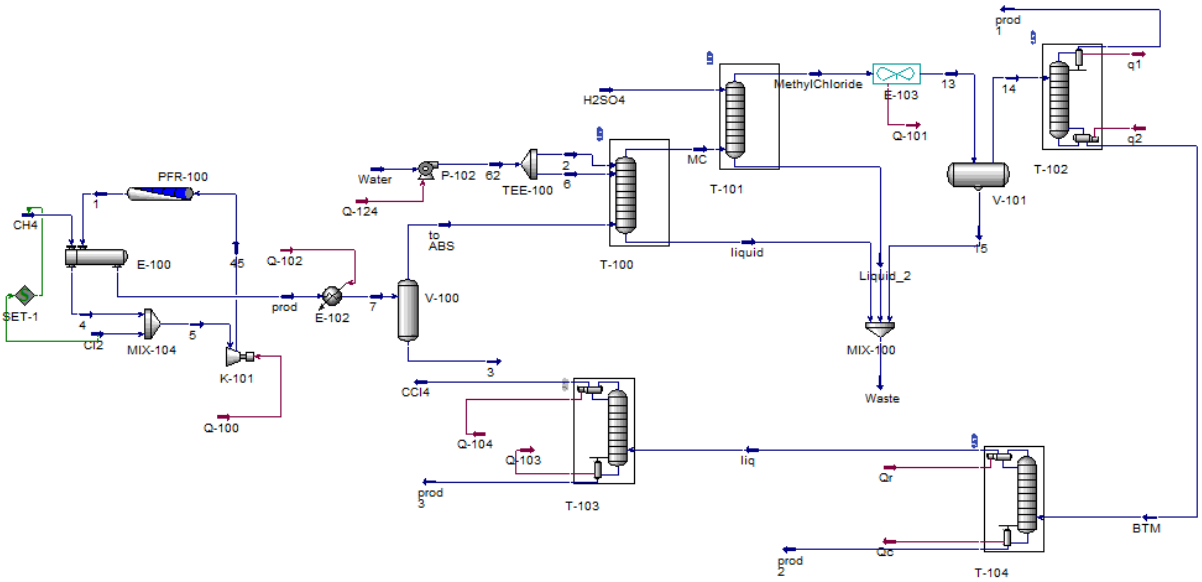

Fig. 1. Aspen HYSYS simulation model (base case) for methylene chloride production process

A sensitivity analysis was performed to assess the effects of operating conditions, such as temperature, pressure, and reactant composition, on methylene chloride production. For process improvement, several measures were undertaken.

4. Economic model

This study, further analyzed the feasibility of the novel process developed from the view of economic performance using the total annual cost (TAC) analysis method. TAC is a key metric for assessing the economic expenses associated with a chemical process, encompassing both total capital costs (TCC) and total operating costs (TOC). The TAC can be calculated using the following formula [10]:

$$TAC = \frac{TCC}{n} + TOC \tag{8}$$

In this equation, n represents the investment payback period, which is typically set at 3 years. Due to the relatively lower costs of pipes, valves, and pumps compared to those of condensers, reboilers, and columns, the capital costs for these items are excluded from the analysis. The capital assessments and formulas are presented in Table 2. The calculation of capital costs for reactors differs somewhat from that of other process equipment due to the unique operational and structural characteristics inherent to reactor design. Specifically, Equation 8 is employed to determine the capital cost associated with a plug flow reactor (PFR). This equation takes into account various factors such as reactor volume, material of construction, and specific design features that contribute to the overall cost assessment. By utilizing this equation, a more accurate estimation of the capital investment required for the implementation of a plug flow reactor within a given process can be achieved, thereby facilitating comprehensive economic evaluations and decision-making in process design [11].

$$\text{Capital Cost} = a + bS^{n} \tag{9}$$

The coefficients for the plug flow reactor equation are as follows: $a = 1400$, $b = 1550$, and $n = 0.7$. The parameter S represents the unit of equipment size, specifically defined as the reactor volume. For this analysis, the reactor volume is considered to be 5 m3. These coefficients and the designated reactor volume play a crucial role in determining the performance and efficiency of the plug flow reactor within the specified process framework.

Table 2. The capital assessments formulas and utility price [10]

Parameter	**Calculation**
Columns ($)	$Capital\ \ \mathrm{Cos}t = 17640 \times D^{1.066} \times H^{0.802}$ $H = 1.2 \times 0.61 \times (N_T - 2)$ where D (diameter) and H (height) are in m.
Reboilers ($)	$A = \frac{Q}{k \times \Delta t}$ $\Delta t = Stream\ Temp. - Column\ base\ Temp.$ $Capital\ \ \mathrm{Cos}t = 7296 \times A^{0.65}$ $heat\ transfer\ coefficient\ \left(kW.K^{-1}m^{-2}\right):\ =\ 0.568$ where Q is heat exchangers duty (kW), k is the heat transfer coeffient and Δt is the temperature difference (K).
Condensers and Coolers ($)	$A = \frac{Q}{k \times \Delta t}$ Δt = log-mean temperature difference of inlet and outlet temperature differences $Capital\ \ \mathrm{Cos}t = 7296 \times A^{0.65}$ $heat\ transfer\ coefficient\ \left(kW.K^{-1}m^{-2}\right):\ =\ 0.852$ where Q is heat exchangers duty (kW), k is the heat transfer coeffient and Δt is the temperature difference (K).
Compressors and Pumps ($)	$7364 m_s \left(\frac{P_0}{P_i}\right)\left(\frac{\eta}{1-\eta}\right)$ where p_0 is the compressor/pump outlet pressure (kPa), P_i is the compressor/pum pressure (kPa), m_s is the inlet mass flowrate of compressor/pump (kg/s), and η is the compressor/pump efficiency
Utillity ($)	LP stream: $5 per ton Cooling water: RMB. $2.5 per ton HP Steam: RMB. $10 per ton Electricity: $0.1 per kwh

5. Results and discussion

This section discusses practical challenges utilizing the process plant simulation model created in this study.

5.1. Steady-state simulations and sensitivity analysis

The simulation model has been employed to conduct material and energy balances for the entire process plant. The steady-state simulation model serves as a tool for optimizing energy use, assessing economic performance, and conducting safety calculations. Prior to evaluating performance, it is essential to validate the simulation model. This can be achieved through sensitivity analysis [12].

The sensitivity analysis focuses on process parameters such as operating conditions, including temperature, pressure, and reactant composition, that affect methylene chloride production. In Aspen HYSYS V11, the sensitivity analysis is conducted using the case studies tool, which allows for the selection and manipulation of various variables and parameters. This tool facilitates the examination of how changes in independent variables impact the dependent variable responses. In the first case study, the influence of reactor inlet temperature on conversion and selectivity was examined by varying the temperature from 100˚C to 500˚C. As illustrated in Fig. 2, it was found that increasing the reactor operating temperature resulted in a decrease in the conversion rate of reaction (2). The findings indicate that the optimal operating temperature is 280˚C, aligning with existing literature trends.

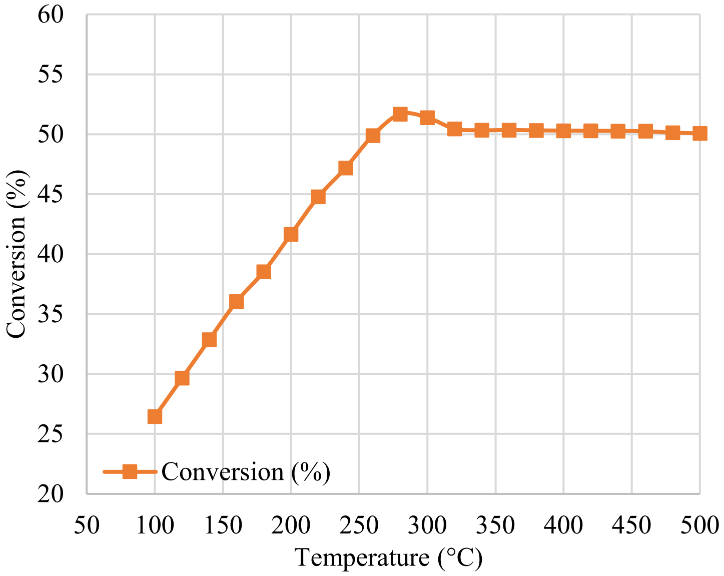

Fig. 2. Effect of reactor temperature on conversion of methyl chloride

The second case study analyzed how conversion rates respond to changes in reactor pressure, with the reactor pressure being the independent variable (as shown in Fig. 3). Pressure was varied between 1 bar and 5 bar, revealing that the optimal pressure for the reaction is 2 bar.

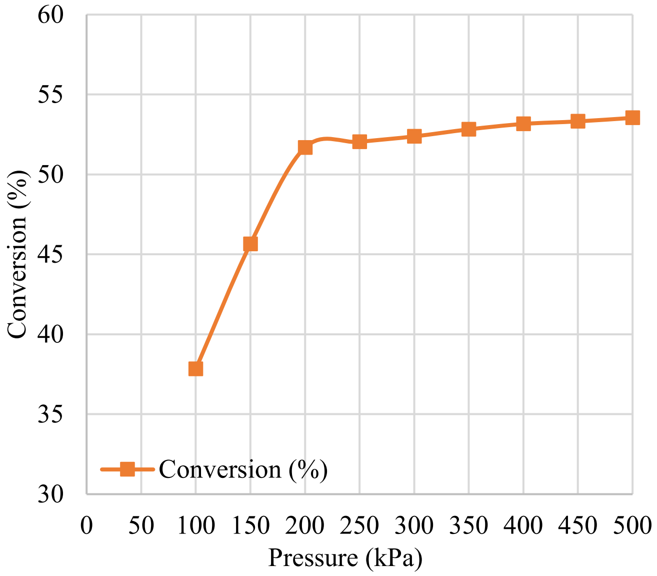

Fig. 3. Effect of reactor pressure on the conversion of methylene chloride

The third case study assessed product distribution and conversion of methyl chloride by altering the reactant composition through adjustments to the CH_4/Cl_2 ratio within the SET-1 operation. This ratio ranged from 0.25 to 1. As the CH_4/Cl_2 ratio increased, the conversion rate decreased, as demonstrated in Fig. 4. These results closely align with literature values.

Overall, the responses generated by the process simulation model under varying operating parameters confirm that the developed model effectively replicates the behavior of the actual process plant and successfully identifies key performance indicators, such as reactor temperature, reactant composition, and heat duties in the reboiler and condenser.

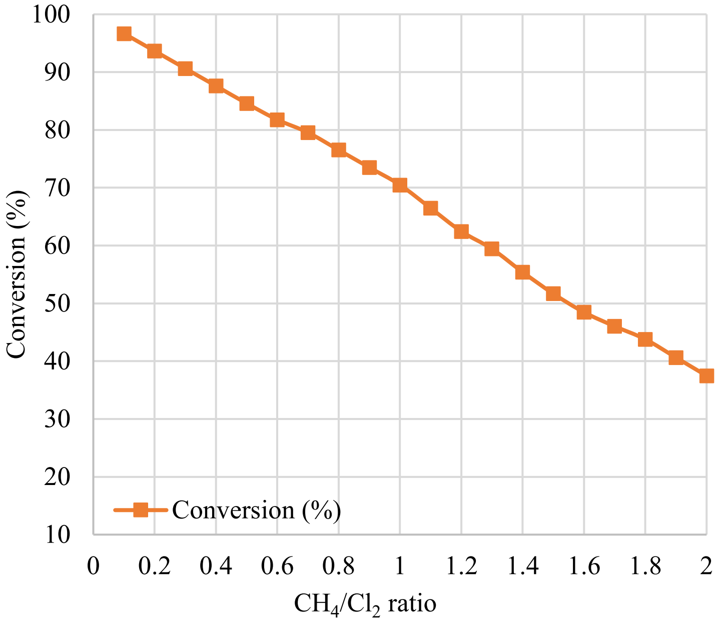

Fig. 4. Effect of methane-chlorine composition on product conversion

Gas Hourly Space Velocity (GHSV) is a fundamental parameter in catalytic reactor design, defined as the volumetric flow rate of feed gas divided by the catalyst bed volume (h^{-1}). This critical metric directly impacts gas residence time, reaction conversion, and overall reactor efficiency. Optimizing GHSV is essential to balance reaction kinetics, mass transfer limitations, and process scalability.

In this section, we systematically evaluate GHSV effects on reactor performance to identify the optimal value for PFR-100 gas-phase reactor. The analysis considers trade-offs between conversion efficiency (favored by lower GHSV) and operational throughput (favored by higher GHSV), providing actionable insights for both laboratory and industrial applications. According to Fig. 5 the optimal GHSV of $200h^{-1}$ was selected PFR-100 reactor based on a systematic evaluation of the space velocity's impact on reactor performance. Intermediate GHSV values balance residence time and throughput, avoiding the inefficiencies of extremely low (kinetically limited) or high (mass-transfer limited) flow regimes. This choice aligns with lab-scale reactor objectives, where conversion efficiency is prioritized over industrial-scale flow rates. The GHSV optimization for the PFR-100 reactor was conducted under the assumptions as listed in Table 3.

Table 3. GHSV analysis assumptions and parameters

Parameter	Capital Costs ($)	Rationale
Catalyst Volume	2.5 m³	Accounts for dead zones in PFR design; ensures active site availability
Catalyst Type	γ-Al_2O_3 pellets	Standard support for chlorination catalysts; high thermal stability
Bulk Density	850 kg/m³	Typical for γ-Al_2O_3-packed beds
Void Fraction (ε)	0.45	Standard for random spherical packing; ensures realistic residence time
GHSV Calculation		Standard definition for gas-phase systems
Key Constraints	Isothermal (280˚C) Constant pressure (2 bar) No catalyst deactivation	Simplifies sensitivity analysis; focuses on GHSV effects
GHSV Range Tested	10–1350 h⁻¹	Covers lab-to-pilot scale transitions

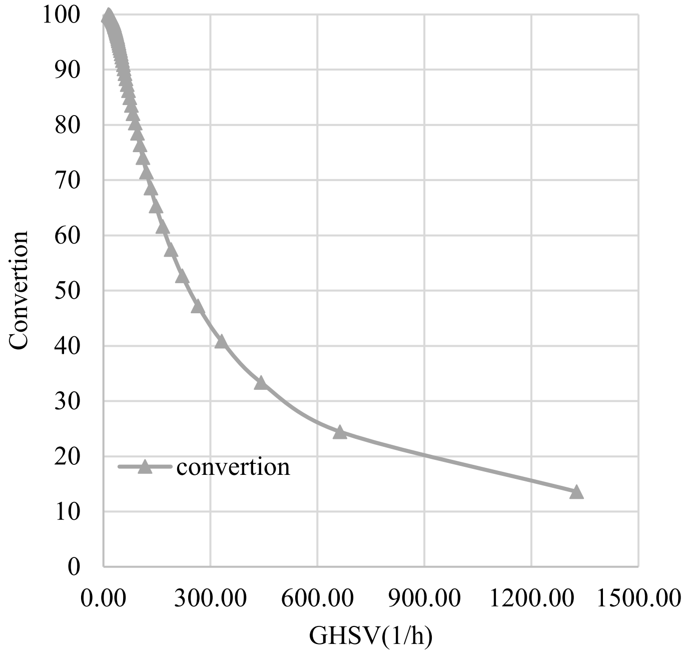

Fig. 5. Effect of methane-chlorine composition on product conversion

5.2. Economic analysis results

In this section, we present an economic evaluation based on the relationships outlined in Table 1. The analysis aims to quantify the financial implications associated with the developed process, focusing on key parameters such as total capital costs (TCC) and total operating costs (TOC). By employing established economic models and methodologies, we will assess the feasibility and profitability of the proposed system. This evaluation not only highlights the potential economic viability of the process but also provides insights into optimizing investment and operational strategies. The findings from this analysis will serve as a foundational reference for further discussions on enhancing process efficiency and sustainability [13].

The results of the total annual cost analysis are presented in Fig. 6, while the operating cost findings are detailed in Fig. 7. These figures illustrate the breakdown of various cost components associated with the process, providing a comprehensive overview of the economic landscape. In Fig. 7, the total annual costs highlight the significant contributions of capital expenditures alongside operating expenses, allowing for a clear understanding of where the largest financial impacts lie. A closer examination of the data reveals that optimizing certain variables can lead to substantial cost savings, emphasizing the importance of efficient resource management. Meanwhile, Fig. 7 focuses specifically on the operating costs, shedding light on the key factors that drive day-to-day expenditures within the process. The analysis indicates that areas such as energy consumption and maintenance play critical roles in influencing overall operational efficiency. By addressing and optimizing these factors, it becomes possible to enhance the economic performance of the process significantly.

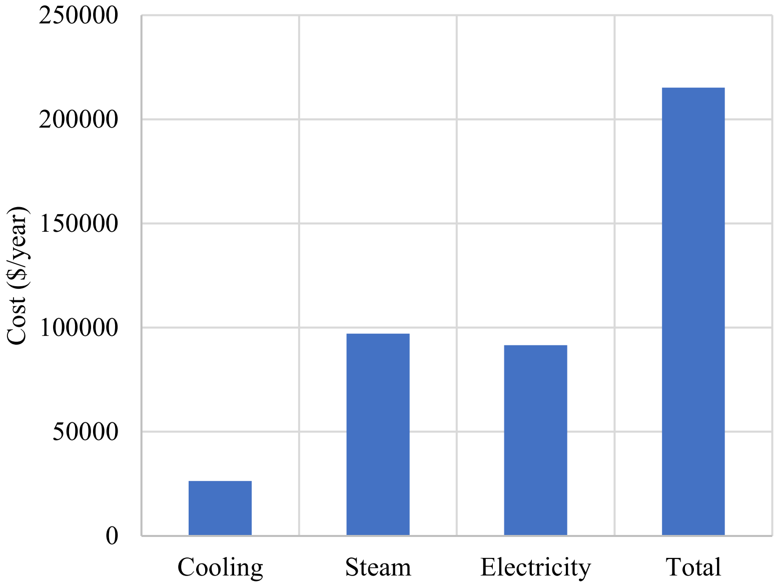

Fig. 6. Breakdown of operating costs for methylene chloride production

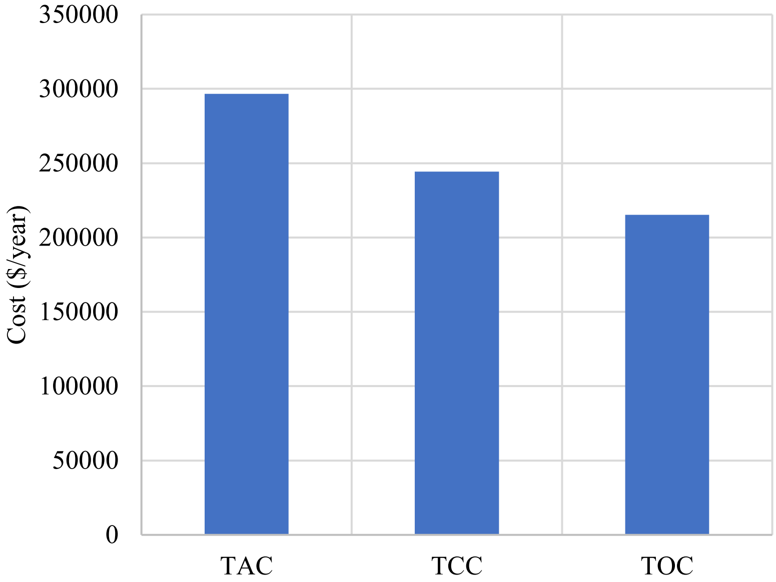

Fig. 7. Economic performance analysis results

Together, these insights underscore the necessity of ongoing economic assessments to ensure the process remains competitive and viable. Future discussions will explore potential strategies for further minimizing costs while maximizing output and sustainability. Based on the data presented in Fig. 7, the total annual cost associated with a production capacity of 1700 tons of methylene chloride per year is approximately $297,000. Additionally, this production unit generates several valuable by-products, including methyl chloride, carbon tetrachloride, and chloroform. The presence of these by-products contributes significantly to the overall profitability of the facility, enhancing its economic viability and operational sustainability.

Table 4. Summary of economic analysis (Base Case: 1700 t/y Capacity and n = 3)

Equipment	Capital Costs ($)
Reactor	$65830
Columns	$105220
Heat Exchangers	$30160
Compressors & Pumps	$44079
TCC	$245289

5.3. Comparative analysis with literature

To validate the simulation model and economic assessment, this study's key outcomes—optimal conditions (280°C, 2 bar), product purity (99% Methylene Chloride), and TAC ($297,000/year for 1,700 t/y)—were benchmarked against recent literature (Table 5).

Table 5. Performance comparison with similar processes

Parameter	T-100	Yandrapu & Kanidarapu [5]	Kim et al. [8]
Reactor temp.	280°C	350°C	300°C
Pressure	2 bar	1.013 bar	1.5 bar
MC purity	99%	98%	96%
Convrsion	51.68%	36.2%	41.5 %
TAC	$297000	$308000	$310000
Energy saving	19%	Baseline	11%

Costs normalized to 1,700 t/y capacity and 2025 USD

6. Conclusion

This study presents a detailed simulation and economic feasibility analysis of the methylene chloride production process via methane chlorination. The findings underscore the significance of optimizing both process design and operational parameters to enhance the overall efficiency and sustainability of the production unit. Methylene chloride, a critical intermediate chemical, not only meets increasing global market demands but also presents the opportunity for considerable economic benefits through the utilization of by-products such as methyl chloride, carbon tetrachloride, and chloroform. The simulation conducted using Aspen HYSYS V11 demonstrated the effectiveness of the developed process model in replicating actual industrial operation behaviors. Key parameters, including reactor temperature, pressure, and reactant composition, were systematically assessed via sensitivity analysis, revealing critical insights into their influence on conversion rates and product yields. Specifically, it was determined that an optimal reactor temperature of 280°C and a pressure of 2 bar significantly enhance the conversion efficiency in the methane chlorination process. The control of the methane-to-chlorine ratio was also identified as a crucial factor in maximizing production efficiency, highlighting the importance of rigorous operational adjustments.

Economically, the analysis of total annual costs revealed a significant investment requirement of approximately $297,000 for a production capacity of 1700 tons of methylene chloride per year. Importantly, the production of valuable by-products not only offsets costs but also improves overall profitability, demonstrating the viability of integrating by-product recovery into chemical manufacturing processes. The analysis detailed in this study emphasizes the necessity for continuous evaluation of production processes as a means of enhancing economic performance and sustainability.

Looking forward, it is essential for industries involved in methylene chloride production to adopt innovative methodologies and frameworks, such as sustainable design principles and advanced process systems engineering approaches, to overcome existing operational challenges. Implementing these strategies can decrease the time required for process conceptualization and allow facilities to operate more safely with reduced environmental impact over their operational lifespan. In conclusion, this study provides a comprehensive framework for both enhancing the efficiency of methylene chloride production and ensuring its economic sustainability. The insights gained can serve as a foundation for developing more effective and environmentally friendly manufacturing processes in the chemical sector. Future research should focus on integrating advanced technologies and methodologies to further improve production efficiency while minimizing environmental impacts, thus paving the way for a more sustainable chemical industry.

References

[1] Salsabila, E., Aisyah, F.A., Cahyani, R.S., Chinara, N.A., 2025. Optimization of methyl chloride production from methanol and hydrogen chloride by enhancing purity and reducing total energy demand. Journal of Chemical Engineering Research Progress, 2(1), 41–50. https://doi.org/10.9767/jcerp.20309

[2] McBee, E.T., Hass, H.B., Neher, C.M., Strickland, H., 1942. Chlorination of methane. Industrial & Engineering Chemistry, 34(3), 296–300. https://doi.org/10.1021/ie50387a009

[3] Rozanov, V.N., Treger, Y.A., 2010. Kinetics of the gas-phase thermal chlorination of methane. Kinetics and Catalysis, 51(5), 635–643. https://doi.org/10.1134/S0023158410050034

[4] Gollangi, R., K, N., 2022. Energy, exergy analysis of conceptually designed monochloromethane production process from hydrochlorination of methanol. Energy, 239, 121858. https://doi.org/10.1016/j.energy.2021.121858

[5] Yandrapu, V.P., Kanidarapu, N.R., 2021. Process design for energy efficient, economically feasible, environmentally safe methyl chloride production process plant: Chlorination of methane route. Process Safety and Environmental Protection, 154, 360–371. https://doi.org/10.1016/j.psep.2021.08.027

[6] Yandrapu, V.P., Kanidarapu, N.R., 2022. Energy, economic, environment assessment and process safety of methylchloride plant using Aspen HYSYS simulation model. Digital Chemical Engineering, 3, 100019. https://doi.org/10.1016/j.dche.2022.100019

[7] Li, Q., Meidan, D., Hess, P., Añel, J.A., Cuevas, C.A., Doney, S., et al., 2023. Global environmental implications of atmospheric methane removal through chlorine-mediated chemistry-climate interactions. Nature Communications, 14(1), 4045. https://doi.org/10.1038/s41467-023-39794-7

[8] Kim, Y., Woo, Y., Park, H., Kim, Y., Chae, H.-J., Park, M.-J., 2022. Kinetic modeling of direct methane chlorination in both free-radical and catalytic reactions. Industrial & Engineering Chemistry Research, 61(6), 2434–2442. https://doi.org/10.1021/acs.iecr.1c04009

[9] Li, D., Shen, J., Zhang, J., Chai, Y., Xie, Y., Qiu, C., et al., 2022. Photocatalytic chlorination of methane using alkali chloride solution. ACS Catalysis, 12(12), 7004–7013. https://doi.org/10.1021/acscatal.2c01228

[10] Lian, L., Liu, W., Liu, S., Wang, H., Cheng, L., Jiang, Y., 2023. Retrofit of the acid gas sweetening process for the refinery based on exergy analysis method. Separation and Purification Technology, 315, 123629. https://doi.org/10.1016/j.seppur.2023.123629

[11] Al-Lagtah, N.M.A., Al-Habsi, S., Onaizi, S.A., 2015. Optimization and performance improvement of Lekhwair natural gas sweetening plant using Aspen HYSYS. Journal of Natural Gas Science and Engineering, 26, 367–381. https://doi.org/10.1016/j.jngse.2015.06.030

[12] Dagde, K., Ayotamuno, I., Nwokoma, D., 2025. Simulation of fluid catalytic cracking unit for optimum production of gasoline using Aspen HYSYS. Journal of Chemical and Petroleum Engineering. https://doi.org/10.22059/jchpe.2025.375055.1506

[13] Yan, X., Sun, J., Yao, S., 2025. Design, thermodynamic and economic analysis, and optimization of a carbon capture integrated energy system for LNG-powered ships. Applied Thermal Engineering, 267, 125728. https://doi.org/10.1016/j.applthermaleng.2025.125728