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Research Article

Optimization of Methyl Chloride Production from Methanol and Hydrogen Chloride by Enhancing Purity and Reducing Total Energy Demand

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Abstract

Methyl chloride, also known as chloromethane, is an important basic material in the global chemical industry. In 2022, the demand for methyl chloride in Indonesia was recorded at 103,748 tons per year. Based on projections, this figure is expected to increase to 134,696 tons per year by 2027. This study aims to investigate the design of methyl chloride plant by considering the efficiency in terms of energy and purity of yield by utilizing Aspen HYSYS V12 simulation tool in process integration. This research utilizes the iterative simulation method to compare the basic process simulation and the modified process simulation for methyl chloride production. The results show that the modified methyl chloride production process simulation has high energy efficiency as indicated by less energy requirements compared to the basic methyl chloride process. In addition, the simulation results of the modified methyl chloride production process produced methyl chloride reaching a high percentage of purity. In the basic process, the purity of methyl chloride reached 72.36% while the modified process showed an increase to 79.51%. It can be concluded that the simulation results of the modified process are more effective than the basic process in terms of energy requirements and purity product

Keywords: Aspen HYSYS; methyl chloride; hydrochlorination; energy efficiency; process integration

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1. Introduction

Methyl chloride, also known as chloromethane, is an important basic material in the global chemical industry. The industries that use methyl chloride the most are silicon manufacturing [1], methylating agents in organic synthesis [2], agricultural fumigation [3]. Due to these various applications, the demand for methyl chloride continues to grow every day, especially in developing countries including Indonesia [4].

In 2022, the demand for methyl chloride in Indonesia was recorded at 103,748 tons per year. Based on projections, this figure is expected to increase to 134,696 tons per year by 2027 [5]. Although demand continues to increase, domestic methyl chloride production is still not sufficient to meet these needs, so Indonesia still imports 22,435 tons of methyl chloride per year [6]. Therefore, the plan to build a methyl chloride plant in Indonesia is very important to meet domestic needs and reduce dependence on imports and even to make Indonesia a methyl chloride exporting country. Thus, the construction of an efficient methyl chloride plant in Indonesia needs to be considered.

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Methyl chloride is produced through two methods. The first method is methane chlorination which involves the reaction of methane (CH_4) with chlorine (Cl_2) at high temperature and pressure to produce methyl chloride [4]. Chlorination of methane involves the following reaction [7]:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \quad \Delta H^{\circ}_{298K} = -99.8 \text{ kJ/mol} \quad (1)$$

The second method is methanol hydrochlorination, where methanol (CH_3OH) reacts with hydrogen chloride (HCl) to form methyl chloride [8]. Methanol hydrochlorination can be represented by the following equation [9]:

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O \quad \Delta H^{\circ}_{298K} = -30.6 \text{ kJ/mol} \quad (2)$$

Kim *et al.* [10] conducted research on methyl chloride production. The simulation used in this study is a DFT (Density Functional Theory) calculation, which is performed at the M06/6-31G(p,d) level of theory to calculate the activation energy of the C-H bond by varying the charge of the Cl atom in the model system. In addition, DFT calculations were also performed for the C-H activation transition state structures of CH_4 and CH_3Cl in the gas phase and on the STO surface. The research included testing the catalyst performance at various reaction temperatures, with varying purity results. At 300 °C, the purity reached 5.6%, while at 350 °C, the purity increased to 22.3%. The study also noted that the product distribution showed a significant proportion for CH_3Cl, with carbon balance results reaching 100% at all temperatures tested. The STO catalyst showed better performance than the blank test and SnO_2 under the same conditions. There are still few previous studies that examine the modification of the methanol hydrochlorination process by recycling the lower yield output of hydrochlorination. Recycling of the bottom output can be done by adding one absorber unit and one decanter separator unit. This process modification can increase methyl chloride production while minimizing energy use.

Jeon [9] explored the integration of methane chlorination and methanol hydrochlorination, which can further maximize the conversion of chlorine gas in methyl chloride production. This integrated approach can overcome current process limitations by utilizing the strengths of both methodologies to improve overall efficiency and product quality. Despite these advances, there is still a significant research gap in recycling the low-yield output of the hydrochlorination process. The integration of an absorbent unit and a decantation separator unit has been proposed to effectively recycle this output, thereby increasing overall methyl chloride production while minimizing energy consumption. This study aims to investigate the design of methyl chloride plant considering energy efficiency and yield purity by utilizing Aspen HYSYS V12 simulation tool in process integration. A conceptual simulation model was developed to produce methyl chloride through methanol hydrochlorination process. To improve the production of methyl chloride in terms of product quality, this study adopts a sustainable design approach with a focus on optimizing energy use in the industrial sector.

2. Methods

The process used is a methyl chloride production process obtained from a related patent. The basic model was designed to accommodate a methanol requirement of 45,000 tons per year as the annual feed rate required in the process with an energy requirement of 1.421×10^7 kJ/h. The process involves the reaction between methanol and chlorine at high temperature to produce methyl chloride [1]. Information on the process design and its operating parameters were taken from the patent as the basis for the initial design.

The process was simulated using Aspen HYSYS V12 simulator software to evaluate its energy requirements and purity yield. Aspen HYSYS is an essential process modeling software in the design, optimization and simulation of processes in the oil, gas, refining and air separation industries developed by AspenTech. Aspen HYSYS provides flexible and easy-to-use modeling of distillation columns, supported by a thermodynamic foundation for accurate calculation of physical properties, transport, and phase behavior. It has a complete library of unit operation models, including distillation, reactors, heat transfer, and controllers in both fixed and dynamic environments. Process simulation is used for the design, analysis, and optimization of technical processes, with software-based model representations that leverage an understanding of chemical and physical properties. Simulation enables evaluation of alternative conditions or systems that are not yet available, hazardous, or in the design stage [11].

In this study, simulations were conducted to understand the performance of the basic process and then modifications were made. The objective of these modifications was to reduce the energy requirements and purity yield of the basic process. Energy efficiency can be calculated as the difference between the heat balance out of the system and the heat balance into the system. Qnet can be written with Equation (3):

$$Qnet = Qout - Qin \quad (3)$$

In addition, the %Purity can be calculated as the ratio between the product mole fraction and the total mole fraction. The calculation of %Purity can be calculated by equation (4):

$$\%Purity = \frac{\text{(mole fraction of product)}}{\text{(total mole fraction)}} \times 100\% \quad (4)$$

The modifications were made using the tools and features in Aspen HYSYS to evaluate their impact on energy efficiency. The method used to improve energy efficiency in this process involved implementing a heat integration strategy using heat exchangers to utilize the heat energy released from the product stream to heat the reactor feed. It also involves adjusting the operating conditions by keeping the pressure in the separation system constant from start to finish. Low energy equipment such as decanters [12] and absorbers are used to reduce overall process energy consumption. The unreacted feedstock recycle system was also redesigned to reduce the consumption of new materials [13] without compromising the purity of the main product. This approach ensures better energy efficiency while improving yield purity.

3. Results and Discussion

3.1 Basic Process Description and Simulation

Basic process simulations in the literature show the production of methyl chloride as the main product of the hydrochlorination reaction [14]. The results of the simulated process based on the literature can be seen in Figure 1 and the Aspen HYSYS simulation in Figure 2 and Table 1. The methyl chloride production process uses a reactor operating at 105 ℃ and 3 bar pressure. The inputs of HCl and methanol are 11423.9 kg/h and 16255.6 kg/h, respectively, at a capacity of 45,000 tons/year at 40 ℃ and molar ratio of 0.8-0.95.

The Peng-Robinson thermodynamic model is a parameter that is often used to estimate the thermodynamic properties of pure compounds and mixtures [15]. For calculations on various phases, the Peng-Robinson thermodynamic model was chosen for this process as in Equation (2) with data on enthalpy of formation of standar (ΔHf° 298) [16] are CH_3OH = -200.9 kJ/mol; HCl = -92.3 kJ/mol; CH_3Cl = -82.0 kJ/mol; and H_2O = -241.8 kJ/mol. Meanwhile, standard entropy data (ΔS° 298) [16] are CH_3OH = 239.7 J/mol.K; HCl = 186.8 J/mol.K; CH_3Cl = 234.18 J/mol.K; and H_2O = 188.72 J/mol.K. Calculation of enthalpy of change of reaction is obtained [16]:

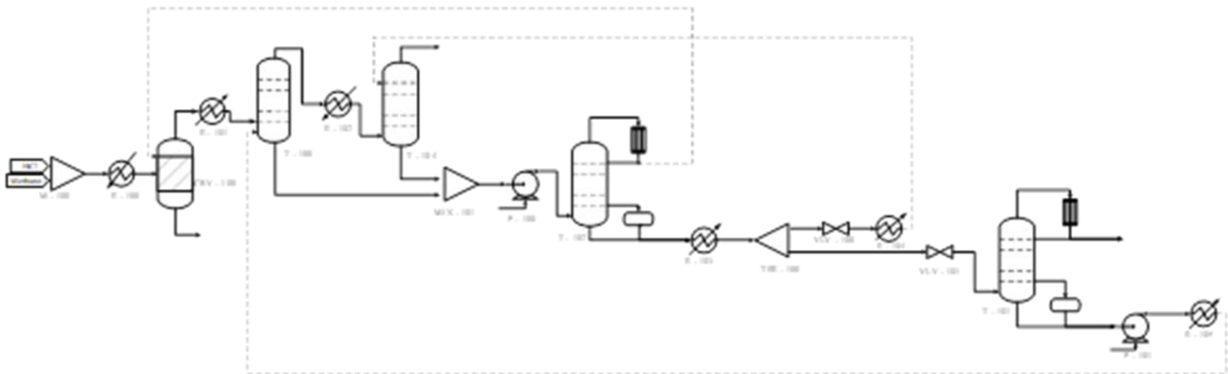

Figure 1. Flowchart of the basic (unmodified) process of methyl chloride production [14]

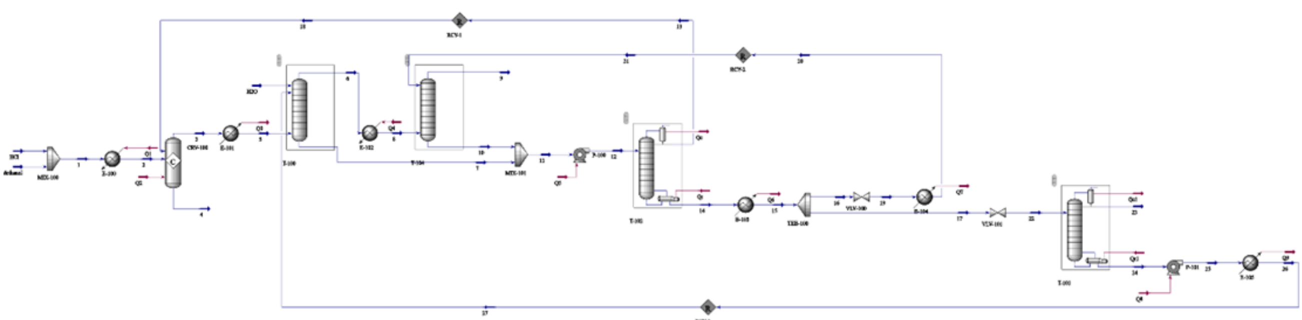

Figure 2. Aspen HYSYS simulation model for methyl chloride production process (without modification)

$\Delta Hrx = \Sigma \Delta Hf^\circ(\text{products}) - \Sigma \Delta Hf^\circ(\text{reactants})$
$\Delta Hrx = [\Delta Hf^\circ(CH_3Cl) + \Delta Hf^\circ(H_2O)] - [\Delta Hf^\circ(CH_3OH) + \Delta Hf^\circ(HCl)]$
$\Delta Hrx = [(-82.0) + (-241.8)] - [(-200.9) + (-92.3)]$ kJ/mol
$\Delta Hrx = -30.6$ kJ/mol

Calculation of entropy of reaction change is obtained:

$\Delta Srx = \Sigma \Delta S^\circ(\text{products}) - \Sigma \Delta S^\circ(\text{reactants})$
$\Delta Hrx = [\Delta S^\circ(CH_3Cl) + \Delta S^\circ(H_2O)] - [\Delta S^\circ(CH_3OH) + \Delta S^\circ(HCl)]$
$\Delta Hrx = [234.18 + 188.72] - [239.7 + 186.8]$ J/mol.K
$\Delta Hrx = -3.6$ J/mol.K

Calculation of Gibbs energy of enthalpy change:

$\Delta Grx = \Delta Hrx - T\Delta Srx$
$\Delta Grx = (-28.49 \text{ kJ/mol}) - (298 \text{ K})(0.0036 \text{ kJ/mol.K})$
$\Delta Grx = -39.22$ kJ/mol

This process is equipped with a mixer, reactor, absorber, splitter, and distillation column to produce methyl chloride. Where the feed in the form of methanol and HCl is homogenized using a mixer and then purified into a product in the reactor. The reactor is the core of a chemical process as a place to convert feed into a product. A reactor equipped with a mixer can optimize the mixing of reactants [17]. In this simulation, the reactor used is a fixed bed reactor that can react reactants in the gas phase [18]. The temperature in the reactor and the entire operation is conditioned using heat exchangers in the form of heaters and coolers. Next is the product separation process to produce high purity methyl chloride products using separators such as absorbers and distillation columns.

The distillation column is an important operating unit for multicomponent separation and the efficiency of multicomponent separation depends on the configuration of distillation sequences [19]. In the process simulation, the operating conditions of the first distillation column were set at a pressure of 3.11 bar at operating temperature. The top product and the remaining unreacted reactants are returned to the reactor to be reacted again, while the bottom product is separated again in the second distillation column at a pressure of 500 mmHg to separate the main product. The lower yield will be returned to the absorber column because it contains a lot of water that can be used as a solvent in the absorber column. The final product methyl chloride is in stream 9 with a mole fraction composition of 0.7236.

3.2 Process Modification to Achieve Energy Efficiency

The production of methyl chloride using basic process simulation is considered less efficient because the final product that still contains reactants is not returned to the design process. In addition, the use of distillation in the process causes the energy required to increase [20], especially if there is a change in pressure in the distillation column. Pressure has a major impact on phase equilibrium in terms of relative volatility, column temperature, and the presence of azeotropes, which affects energy requirements, utility costs, and process configuration [21]. The mass and energy balance from HYSYS simulation of the basic process simulation can be seen in Table S1 (Supporting Information).

The largest energy requirement in the basic process simulation is in the distillation column [22]. This gives an idea to develop the methyl chloride design process by modifying the operation to produce less energy requirements. In this modified process, the operat ing conditions in the reactor and feed are the same as the basic process system. The use of a decanter separator and absorption column allows a decrease in the energy requirements of the process [23]. The process modification can be seen in Figure 3 and Figure 4.

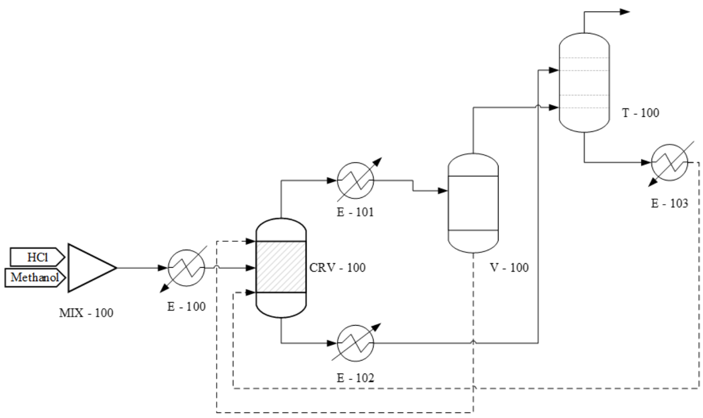

Figure 3. Flowchart of process modification in methyl chloride production

Similar to the basic process simulation, the methyl chloride production process uses a reactor operating at 105 ℃ and 3 bar pressure. The inputs of HCl and methanol are 11423.9 kg/h and 16255.6 kg/h, respectively, at a capacity of 45,000 tons/year at 40 ℃ and molar ratio of 0.8-0.95. The upper product of the reactor is separated based on density differences [24], where the upper product will be separated again using an absorber column, while the lower product which still contains many reactants is returned to the reactor.

In the absorber column, the incoming feed is dissolved with pure H_2O at room temperature of 30 ℃ and pressure of 3 bar. The bottom product of the absorber column is returned to the reactor and the bottom product of the reactor which contains a lot of water is used as a solvent in the absorber column. The final product methyl chloride is in stream 9 with a mole fraction composition of 0.7951.

In the modification of the methyl chloride process, energy requirements have decreased. This is due to the low energy requirement in the decanter separator and absorber column when compared to the energy requirement in the distillation column [25]. Low total energy makes the process more efficient because it supports economic growth [26]. The mass and energy balance from HYSYS simulation of the modified process can be seen in Table S2 (Supporting Information).

Energy requirements can be calculated using Equation (3). Based on the table obtained, the energy value required in the basic process is 1.421×10^7 kJ/h. When compared to the modified process, the energy requirement is 1.362×10^7 kJ/h. Data analysis from Table S1 and Table S2 shows that the energy required in the modified process is smaller than the basic process, proving that the modified process is more efficient than the basic process.

3.3 Analysis of Product Purity

The purity level of the hydrochlorination process, which produces methyl chloride as the main product, is an important indicator of the overall quality of the product produced. By definition, purity is a product yield that is devoid of impurities, contaminants, and foreign matter of any kind [27]. The percentage purity is calculated based on the product mole fraction and total mole fraction values obtained from Aspen HYSYS data. The total mole fraction data in the basic process design can be seen in Table 1. Using the data in Table 1, the purity of methyl chloride can be calculated using Equation (4). Based on the calculation, the main product methyl chloride using the basic process produces a purity percentage of 72.36%. To compare with the modified process, the total mole fraction data on the modified process design can be seen in Table 2. Using the data in Table 2, the purity of methyl chloride can be calculated using Equation (4). Based on the calculation, the main product of methyl chloride using the modified process produces a purity percentage of 79.51%. The comparison results of the two processes can be seen in Table 3.

4. Conclusions

Simulation of a methyl chloride plant capable of producing methyl chloride from the hydrochlorination reaction of methanol was carried out using the Aspen HYSYS process simulator. The modified methyl chloride process

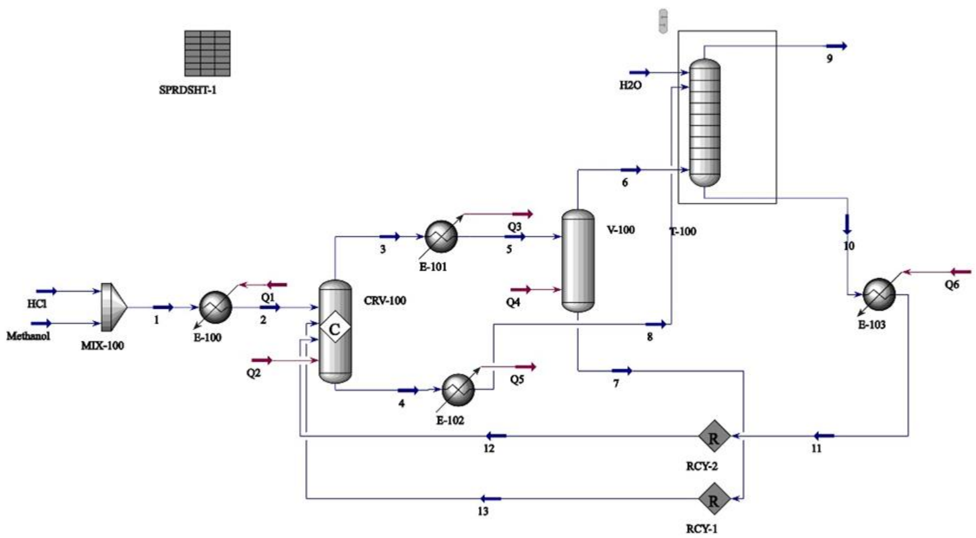

Figure 4. Aspen HYSYS simulation model for modified methyl chloride production process

showed lower energy requirements compared to the basic methyl chloride process. The energy value required in the basic process is 1.421×10^7 kJ/h. When compared to the modified process, the energy requirement is 1.362×10^7 kJ/h. In addition, the methyl chloride produced from the modified process achieved a higher purity percentage. In the basic process, the purity of methyl chloride reached 72.36% while the modified process showed an increase to 79.51%. It can be concluded that the simulation results of the modified process are more effective than the basic process in terms of energy requirements and purity produced. Further research on the economic aspects of the modified methyl chloride process design using process simulators such as Aspen Process Economic Analyzer (APEA) to provide a more comprehensive understanding of the methyl chloride modification from the aspect of its economic feasibility.

CRedit Author Statement

Author Contributions: E. Salsabila: Conceptualization, Methodology, Software, Investigation, Writing, Review, Editing, Supervision; F. Aisyah: Conceptualization, Software, Investigation, Writing, Review, Editing; I. Zulfa: Conceptualization, Investigation, Writing, Review, Editing, Visualization, Project administration; R. Cahyani: Conceptualization, Validation, Investigation, Writing, Review, Editing; N. Chinara: Data Curation, Investigation, Resources. All authors have read and agreed to the published version of the manuscript.

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Table 1. Product composition of the modified process

Composition	Mole Fraction
Methanol (CH_3OH)	0.0000
Hydrochloric Acid (HCl)	0.1797
Methyl Chloride (CH_3Cl)	0.7951
Water (H_2O)	0.0252
Total mole fraction	1

Table 2. Comparison between basic and modified process of the product purity

Process System	Purity of methyl chloride production (%)
Basic process	72.36
Modified process	79.51

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