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Research Article

Improving Process Design for Reaching Energy Efficiency, Environmentally Friendly, and Producing High Purity Methyl Chloride of Dehydrochlorination Process of Methanol and Hydrogen Chloride

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Abstract

Methyl chloride, also known as chloromethane, plays a vital role in producing various industrial goods. The current demand for methyl chloride in Indonesia exceeds production levels, making the design of a methyl chloride plant essential. This research focuses on improving methyl chloride production economically and operationally by exploring plant design using simulations that emphasize energy efficiency and high purity. The objective of this research is to develop a process design for producing methyl chloride from methanol and hydrogen chloride, aiming for energy efficiency, an environmentally friendly factory, and high-purity methyl chloride products. The research employed an iterative simulation method to compare the basic and modified processes for methyl chloride production. The process involved constructing a simulation model using Aspen HYSYS, analyzing the simulation results using Aspen Energy Analyzer V12, and iteratively adjusting process parameters until achieving the desired performance or results. The research findings indicate that the methyl chloride modification process exhibits a lower energy requirement compared to the methyl chloride base process. Moreover, the modification process demonstrates minimal carbon emissions, establishing it as a sustainable and environmentally friendly design. Additionally, the methyl chloride produced in the modification process achieves a higher percentage of purity. In the initial process, the methyl chloride purity stood at 98.17%, while in the modified process, it saw an elevation to 99.35%. Considering these three aspects, the modification process is conclusively more efficient than the basic process system.

Keywords: Aspen HYSYS; dehydrochlorination; iterative simulation method; methyl chloride

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1. Introduction

Methyl chloride or chloromethane is an important chemical for the production of various industrially product. Methyl chloride is used primarily in the manufacture of fuel additives (tetra ethyl lead), bioremediation [1], resins, elastomers, silicone fluid, medicine [2], methyl cellulose [3], and it can be used as a raw material for the industrial floor cleaner [4]. So, the demand of methyl chloride increases every year especially in developing countries, including Indonesia [5]. However, the amount of methyl chloride needed in Indonesia is not yet comparable to methyl chloride produced [6]. Based on the Central Statistics Agency (2020), Indonesia still imports 1.486.874

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tonnes/year of methyl chloride to meet domestic needs. Therefore, it is necessary to design a methyl chloride plant while paying attention to certain aspects.

There are two main industrial processes for the synthesis of methyl chloride: the chlorination of methane and the hydrochlorination of methanol and hydrochloric acid [7]. The hydrochlorination process of methanol and hydrochloric acid operates under lower conditions compared to the chlorination of methane, resulting in reduced energy requirements and costs. Additionally, the hydrochlorination process yields higher and does not involve side reactions, making it the chosen method [8].

The production of methyl chloride through the hydrochlorination process involves reacting methanol with hydrogen chloride in a reactor, as described by previous researchers [4]. However, the current hydrochlorination process lacks an energy efficiency concept, posing challenges for economic sustainability. Additionally, achieving high conversion rates in the production of methyl chloride remains a challenge in the industry, limiting its overall production.

To enhance methyl chloride production from both economic and production perspectives, this research will investigate the design of a methyl chloride plant using simulations that consider aspects of energy efficiency and high methyl chloride purity. Research studies indicate that addressing this issue can be accomplished by implementing sustainable design procedures at various stages of the process. Optimizing energy usage in the industry is crucial, aligning with key targets in the industrial sector. The objective of this research work is to develop a modified process design for producing methyl chloride from methanol and hydrogen chloride, aiming to achieve energy efficiency, establish a factory adhering to environmentally friendly principles, and obtain methyl chloride products with high purity.

2. Methods

The production process model for methyl chloride from hydrochlorination of methanol was designed using Aspen HYSYS, and the corresponding process flow sheet is depicted in Figure 1. This simulation model serves to predict the plant process response through the application of mass and energy balances, phase considerations, and chemical equilibrium relationships. The model incorporates relevant thermodynamic data, real-time operating conditions, and rigorous equipment models to emulate actual factory process [9]. The Aspen HYSYS process simulation tool is employed for designing conceptual simulation models for methyl chloride production, following industry standards. Process information for methyl chloride was sourced from the literature [4]. A conceptual process simulation model was developed specifically for the production of methyl chloride through methanol hydrochlorination. Furthermore, the Aspen Energy Analyzer tool is utilized to analyze energy consumption across all factory processes. Aspen HYSYS is employed for energy efficiency, heat, and methyl chloride production conversion studies. The detailed simulation incorporates measurement operations that reflect real-time concepts of factory industrial processes.

In this research, an iterative simulation method that was utilized to investigate, study, and compare both the basic and advanced processes for methyl chloride production. The iterative simulation method entails repeated iterations using software to adjust process parameters and observe their impact on simulation results. The process was initiated by constructing a simulation model using Aspen HYSYS, analyzing the results with Aspen Energy Analyzer, and iteratively modifying process parameters until the desired performance or results were achieved. The process modifications conducted in the research involved adjusting the process parameters and tools using the iterative simulation method principle. Further details about the modifications made can be found in the next chapter.

In addition, this research involves a comparison between the initial methyl chloride purity and the purity after modification. The mass balance of methyl chloride obtained using Aspen HYSYS. Subsequently, the % Purity is calculated

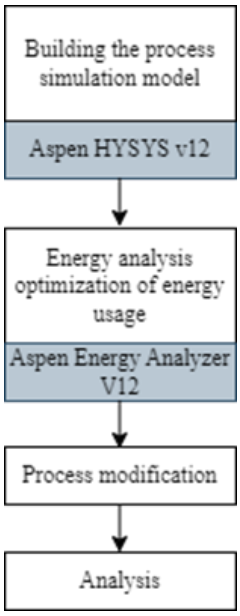

Figure 1. Process integration methodology chart.

as the ratio between the mass of methyl chloride product (kg/h) and the total product mass (kg/h). The % Purity calculation is expressed in Equation (1):

$$\%\ Purity = \frac{Mass\ of\ methyl\ chloride\ product}{Total\ product\ mass} \times 100\% \quad (1)$$

After obtaining data on energy requirements through Aspen Energy Analyzer and product purity, the results were analyzed and compared between the basic process system for producing methyl chloride and the modified methyl chloride process to assess the efficiency of each process.

3. Results and Discussion

3.1. Basic Process Description and Simulation

The concept described in literature serves as the foundation for the methyl chloride processs [10]. Industrial standard methane chlorination plant to produce methyl chloride as the primary product is given in Figure 2, including the Aspen HYSYS simulation results (Figure 3 and Table 1). The reactor is a fixed bed reactor operating under conditions set at 300 ℃ with a pressure of 10 atm. To take into consideration for capable of calculating various phases, the Peng-Robinson thermodynamic model was chosen for the process. The chemistry used for this process is presented in Equation (2):

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O \quad \Delta H°_{298} = -34.7\ kJ/mol \quad (2)$$

The primary reaction involves the production of methyl chloride and water through the interaction of methanol and hydrogen chloride. In addition to this principal reaction, there are two side reactions. The first one produces methyl ether by the reaction of hydrogen chloride and methanol, while the second one involves the combination of hydrogen chloride and methyl ether, resulting in the formation of chloroform [11]. At the operational temperature, the rates of the side reactions are considered to have minimal impact. Consequently, the chemical setup of the reactor does not account for these side reactions [12]. As a result, the composition of the product is predominantly methyl chloride and water and unreacted hydrogen chloride.

There are distillation columns, absorbers, mixer, and a reactor in the process. Mixer and reactor units play a crucial role in homogenizing the mixture during the process of making methyl chloride. The selected reactor type is a fixed bed reactor, known for its efficiency in reacting gas phase reactants. Subsequently, the operating conditions undergo pretreatment or conditioning using a heater or cooler. The formed product then undergoes purification through separation methods, including distillation and absorption.

In summary, the production of methyl chloride involves the reaction of reactants in a

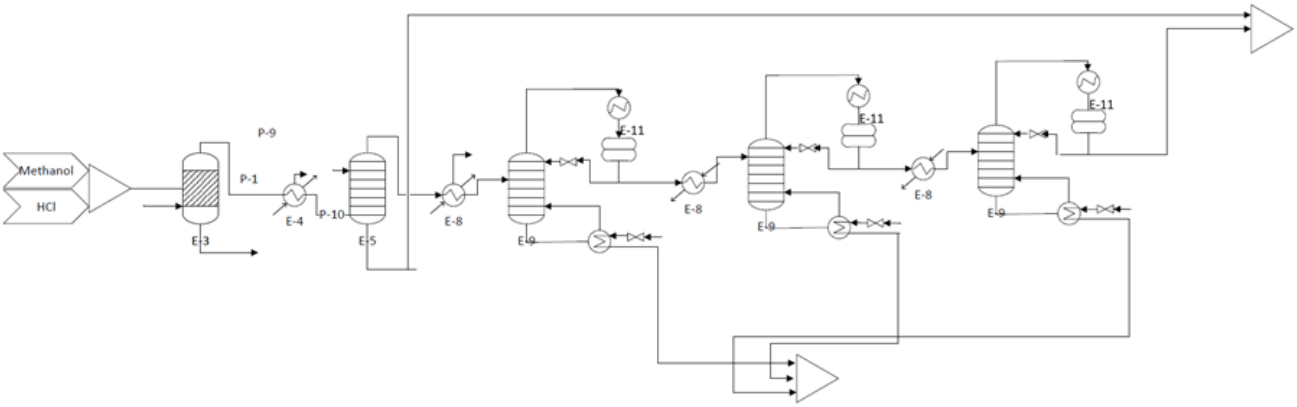

Figure 2. Methyl chloride basic process flow diagram

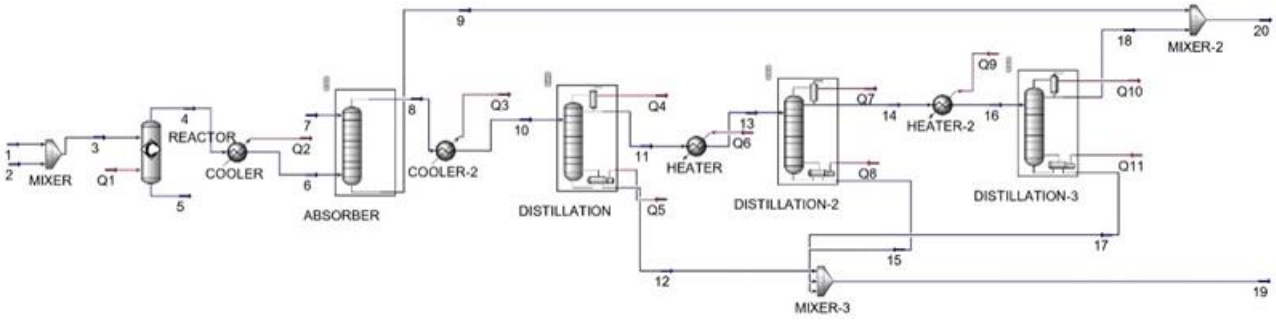

Figure 3. Aspen HYSYS simulation model for basic (unmodified) methyl chloride production process

mixer and reactor, followed by the separation of methyl chloride from other compounds using an absorber. The final step includes the purification of the product through multistage distillation. The process of making methyl chloride will be detailed in the next chapter [26]. The methyl chloride production process using the dehydrochlorination of methanol and hydrogen chloride was simulated in the Aspen HYSYS user interface. The Peng-Robinson equation was selected because it is capable of calculating various phases.

The raw materials, methanol, and hydrogen chloride, undergo a reaction in a mixer at a temperature of 300 °C and a pressure of 10 atm before entering the fixed-bed type reactor (REACTOR). The purpose of the mixer is to homogenize methanol and hydrogen chloride (pretreatment), ensuring a more homogeneous and evenly mixed compound upon entering the reactor [13]. The fixed bed reactor is chosen and operates at a temperature of 300 °C and a pressure of 10 atm. This reactor was chosen for its ability to effectively react with gaseous reactants. The reactor's output gas is then conditioned to operating conditions through a cooler before being directed to the absorber. Within the absorber, residual methanol is separated from other compounds, including a small amount of H_2O, methyl chloride, and residual HCl. A multistage distillation process is employed to further separate these compounds. The distillation process involves separating compounds based on differences in their boiling points [14]. The first distillation process (DISTILLATION) takes place at a temperature of -30.8 °C. HCl has a boiling point of -85.05 °C and methyl chloride has a boiling point of -22.08 °C. In the first distillation, HCl evaporates and exits as a gas product, while methyl chloride is collected as a bottom product (liquid).

The second distillation process (DISTILLATION-2) and the third distillation process (DISTILLATION-3) are conducted to purify the methyl chloride product so that methyl chloride with high purity is obtained. The methyl chloride, in liquid form from the distillation, is combined with the output from previous distillation processes represented in Streams 12, 15, and 17. In this phase, any unused HCl and methanol are directed to the waste processing unit. The final methyl chloride product from this process is found in Stream 19, with a methyl chloride composition of 5,570.06 kg/h.

3.2. Modification of Process for Improving Process Design for Reaching Energy Efficiency and Producing High Purity Methyl Chloride

In general, the production of methyl chloride using this process is not entirely efficient and does not align with a sustainable concept in the design process, as the remaining unreacted HCl is disposed of in the waste processing unit without being reused. Heat energy integration is essential for enhancing waste heat recovery and optimizing the design of utilities in the system to achieve greater energy efficiency. This work was conducted using the Aspen Energy Analyzer,

Table 1. Mass and energy balances of the basic process for methyl chloride production

Material Streams											
		1	2	3	4	5	6	7	8	9	10
Vapour Fraction		1,0000	1,0000	1,0000	1,0000	0,0000	0,1762	0,0000	1,0000	0,0000	0,6917
Temperature	C	300,0	300,0	300,3	300,0	300,0	80,00	30,00	38,46	79,91	30,00
Pressure	kPa	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013
Molar Flow	kgmole/h	126,7	823,2	949,9	949,9	0,0000	949,9	153,6	159,4	944,2	159,4
Mass Flow	kg/h	3997	1,780e+004	2,180e+004	2,180e+004	0,0000	2,180e+004	2768	7338	1,723e+004	7338
Liquid Volume Flow	m3/h	5,002	18,70	23,70	22,70	0,0000	22,70	2,774	8,115	17,36	8,115
Heat Flow	kJ/h	-2,388e+007	-1,676e+008	-1,915e+008	-1,953e+008	0,0000	-2,356e+008	-4,392e+007	-1,429e+007	-2,652e+008	-1,524e+007
		11	12	13	14	15	16	18	17	19	20
Vapour Fraction		0,0000	0,0000	0,6924	0,0000	0,0000	0,9120	0,0000	0,0000	0,0000	0,0476
Temperature	C	-30,35	42,88	-28,00	-31,41	46,06	-30,00	-31,66	29,57	42,88	68,55
Pressure	kPa	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013
Molar Flow	kgmole/h	47,60	111,8	47,60	46,00	1,607	46,00	45,60	0,3985	113,8	989,8
Mass Flow	kg/h	1764	5573	1764	1683	81,13	1683	1664	19,57	5674	1,889e+004
Liquid Volume Flow	m3/h	2,022	6,094	2,022	1,933	8,867e-002	1,933	1,911	2,146e-002	6,204	19,27
Heat Flow	kJ/h	-5,180e+006	-1,191e+007	-4,706e+006	-5,005e+006	-1,678e+005	-4,407e+006	-4,962e+006	-4,213e+004	-1,212e+007	-2,702e+008

Compositions										
	1	2	3	4	5	6	7	8	9	10
Comp Mole Frac (Methanol)	0,9650	0,0000	0,1287	0,0103	0,0108	0,0103	0,0000	0,0000	0,0104	0,0000
Comp Mole Frac (H2O)	0,0350	0,8043	0,7017	0,8201	0,9692	0,8201	1,0000	0,0077	0,9865	0,0077
Comp Mole Frac (HCl)	0,0000	0,1957	0,1696	0,0512	0,0038	0,0512	0,0000	0,2996	0,0010	0,2996
Comp Mole Frac (Refrig-40)	0,0000	0,0000	0,0000	0,1184	0,0161	0,1184	0,0000	0,6927	0,0022	0,6927
	11	12	13	14	15	16	18	17	19	20
Comp Mole Frac (Methanol)	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0099
Comp Mole Frac (H2O)	0,0000	0,0110	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0108	0,9411
Comp Mole Frac (HCl)	0,9569	0,0198	0,9569	0,9903	0,0000	0,9903	0,9981	0,0993	0,0198	0,0469
Comp Mole Frac (Refrig-40)	0,0431	0,9693	0,0431	0,0097	1,0000	0,0097	0,0019	0,9007	0,9695	0,0022

where the necessary data, including streams and hot and cold duties for the entire process, were extracted from Aspen HYSYS. To develop a methyl chloride design process with a sustainable and recyclable concept, a process modification was implemented, as depicted in Figure 4.

The modification of the methyl chloride process design involves initially following the same steps as the base case process system. The differences and innovations in this process are found in the type of reactor, separation, and purification processes. In this modified process, a multistage reactor is employed under the same operating conditions as the base case process system. The use of a multistage reactor ensures complete conversion of the HCl reactant into the desired product.

Subsequently, the product and remaining reactants are directed to a three-phase separator (3 SEP). This separator divides the feed into three parts: methyl chloride with a small amount of H_2O (gas) on top, methyl chloride with a small amount of H_2O as a light liquid, and pure H_2O as a heavy liquid. To separate methyl chloride from H_2O, an absorber is employed. The absorber's output is the methyl chloride product, while the remaining methyl chloride and water are recycled for further reaction in the mixer section, as depicted in stream 18. The final product from this process is represented in stream 13, with a methyl chloride mass of 6,872.67 kg/h.

Compared to the previous methyl chloride design process, the design modification process incorporates a more sustainable concept. This is attributed to the recycling of the remaining unreacted substances in the mixer section for further reaction. Additionally, the mass of the methyl chloride product is higher compared to the base process system. Further comparisons of the process designs from energy and purity aspects are discussed in the next chapter.

3.3. Energy Targeting

Utilizing the Aspen Energy Analyzer simulation, energy requirement data was acquired for both the methyl chloride base process system and the methyl chloride modification process. Subsequently, a comparison of the energy

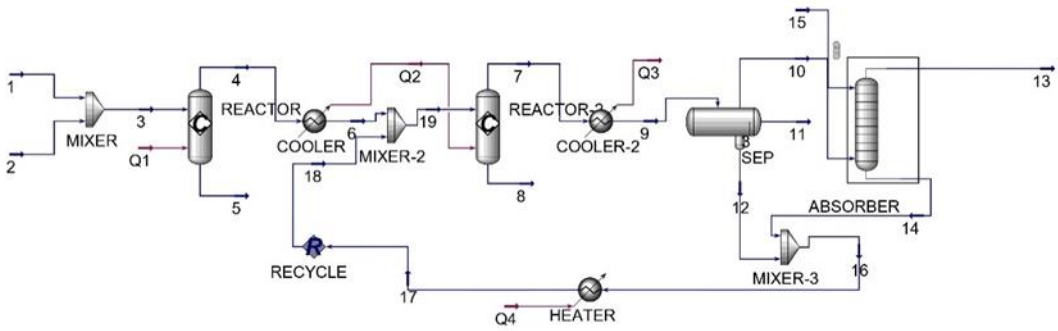

Figure 4. Aspen HYSYS simulation model for the modified methyl chloride production process

Table 2. Mass and energy balances of the modified process for methyl chloride production

Material Streams											
		1	2	3	4	5	6	7	8	9	10
Vapour Fraction		1,0000	1,0000	1,0000	1,0000	0,0000	1,0000	1,0000	0,0000	0,0048	1,0000
Temperature	C	300,0	300,0	299,0	389,0	389,0	300,0	301,3	301,3	100,0	100,0
Pressure	kPa	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013
Molar Flow	kgmole/h	140,8	137,1	277,9	277,9	0,0000	277,9	3,178e+004	0,0000	3,178e+004	153,6
Mass Flow	kg/h	4510	5000	9510	9510	0,0000	9510	5,866e+005	0,0000	5,866e+005	7209
Liquid Volume Flow	m3/h	5,668	5,745	11,41	10,26	0,0000	10,26	592,4	0,0000	592,4	7,854
Heat Flow	kJ/h	-2,631e+007	-1,157e+007	-3,788e+007	-4,105e+007	0,0000	-4,230e+007	-7,332e+009	0,0000	-8,841e+009	-1,549e+007
		11	12	13	14	15	16	17	18	19	
Vapour Fraction		0,0000	0,0000	1,0000	0,0000	0,0000	0,0000	1,0000	1,0000	1,0000	
Temperature	C	100,0	100,0	55,34	100,2	25,00	100,0	300,0	300,0	300,0	
Pressure	kPa	1013	1013	1013	1013	1013	1013	1013	1013	1013	
Molar Flow	kgmole/h	0,0000	3,162e+004	138,6	164,8	149,9	3,179e+004	3,179e+004	3,150e+004	3,178e+004	
Mass Flow	kg/h	0,0000	5,794e+005	6917	2992	2700	5,824e+005	5,824e+005	5,771e+005	5,866e+005	
Liquid Volume Flow	m3/h	0,0000	584,6	7,556	3,004	2,705	587,6	587,6	582,2	592,5	
Heat Flow	kJ/h	0,0000	-8,826e+009	-1,231e+007	-4,608e+007	-4,289e+007	-8,872e+009	-7,358e+009	-7,291e+009	-7,333e+009	

Compositions										
	1	2	3	4	5	6	7	8	9	10
Comp Mole Frac (Methanol)	1,0000	0,0000	0,5065	0,0405	0,0405	0,0405	0,0136	0,0124	0,0136	0,0027
Comp Mole Frac (H2O)	0,0000	0,0000	0,0000	0,4660	0,4660	0,4660	0,9786	0,9867	0,9786	0,1074
Comp Mole Frac (HCl)	0,0000	1,0000	0,4935	0,0275	0,0275	0,0275	0,0000	0,0000	0,0000	0,0000
Comp Mole Frac (Refrig-40)	0,0000	0,0000	0,0000	0,4660	0,4660	0,4660	0,0078	0,0010	0,0078	0,8899
	11	12	13	14	15	16	17	18	19	
Comp Mole Frac (Methanol)	0,0278	0,0136	0,0000	0,0025	0,0000	0,0136	0,0136	0,0136	0,0138	
Comp Mole Frac (H2O)	0,4844	0,9829	0,0179	0,9943	1,0000	0,9829	0,9829	0,9829	0,9784	
Comp Mole Frac (HCl)	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0002	
Comp Mole Frac (Refrig-40)	0,4878	0,0035	0,9821	0,0032	0,0000	0,0035	0,0035	0,0035	0,0076	

requirements for each process is depicted in Figure 5 and Figure 6.

Analysis of data from Figure 5 and Figure 6 reveals that the energy requirements for the base process system exceed those of the modification process. This is evident in the higher value associated with the base process system compared to the modification process. From an energy perspective, it is evident that the modification process is considerably more efficient than the base process system. Additionally, the modification process contributes to smaller carbon emissions compared to the base process system. Consequently, the modification process can be considered more environmentally friendly than the base process system.

3.4. Enhanced Product Purity Analysis

The quality of methyl chloride products serves as an indicator for both the factory and the overall quality of the products manufactured. A higher level of purity in the product corresponds to superior quality in both the product itself and the factory [15]. To determine the percentage purity in the two simulated processes, calculations are conducted using the Equation (1). The masses of the methyl chloride product and the total product mass were obtained from Aspen HYSYS data. The data for the total product mass in the base process design is interpreted in the Table 3. By using this data in Table 3, the calculation of the purity of the methyl chloride in the base process system according to Equation (1) is as follow:

% Purity of basic process = (5570.06 kg/h) / (5674.10 kg/) x100% = 98.17%

Based on the calculation, the methyl chloride produced using the basic process system is estimated to have a purity of 98.17%. To compare this with the modified process, the purity of methyl chloride in the modified process was also calculated using the same method as follow:

% Purity of basic process = (6872.67 kg/h) / (6917.31 kg/) x100% = 99.35%

A comparison between the purity of these products can be shown in Table 4.

Based on the purity data between the base process system methyl chloride production and the modified methyl chloride production (Table 5), it can be compared that the methyl chloride with the modified process has a higher purity with a product purity of 99.35%. With a residual of 1.18% between the two processes.

Table 5. Comparison between the purity of basic and modification process

Purity of methyl chloride basic process system production (%)	Purity of methyl chloride production with modification process (%)
98.17	99.35
Residual	1.18

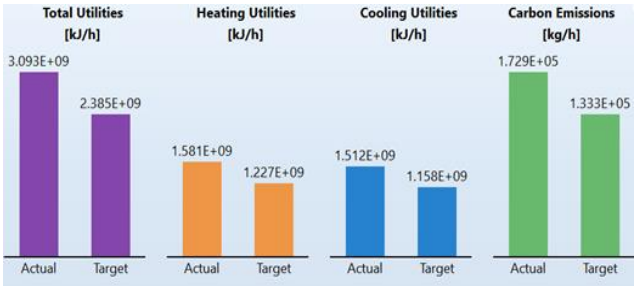

Figure 5. Energy requirements in the methyl chloride basic process system

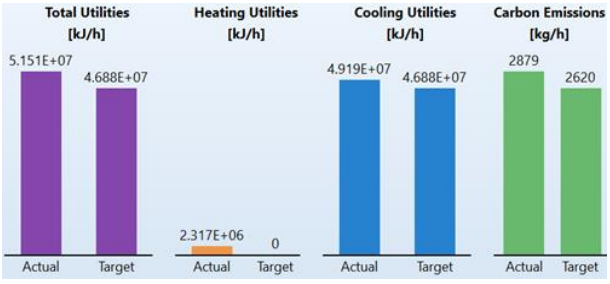

Figure 6. Energy requirement in the modified methyl chloride process

Table 3. Composition of basic process system product

Composition	Mass flow (kg/h)
Methanol	0.00
Water (H_2O)	22.07
HCl	81.97
Methyl Chloride	5,570.06
Total product	5,674.10

Table 4. Composition of modified process product

Composition	Mass flow (kg/h)
Methanol	0.00
Water (H_2O)	44.64
HCl	0.00
Methyl Chloride	6,872.67
Total product	6,917.31

4. Conclusion

The methyl chloride modification process showed lower energy requirements and carbon emissions when compared to the basic methyl chloride process. Moeover, the methyl chloride produced in the modification process achieved a higher purity percentage. By considering these three aspects, the modification process was proven to be more efficient than the basic process and was in accordance with the research objectives. However, this research solely compares the methyl chloride modification process in terms of energy efficiency and product purity, without delving into its economic implications. Future research could further examine the economic aspects of modifying the methyl chloride process design, employing tools such as the Aspen Process Economic Analyzer (APEA). It could also contribute to a more comprehensive understanding of the modification process for methyl chloride and offer insights into its economic viability.

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