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Research Article

Improving 1,2-Ethylene Dichloride Yield and Purity with Reducing Carbon Emissions from Ethylene through Waste Treatment Method Modification

M. Syauqi Finardhy Saputra*, Rheka Fauzan Azhar, Try Ramadhani, Vares Dodi

Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang, Indonesia.

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Abstract

1,2-ethylenedichloride (EDC) is a chemical compound used widely in industry. This study aims to develop a modified process for EDC production through direct chlorination and oxychlorination methods to improve mass efficiency, establish an environmentally friendly plant, and produce high purity products. Conceptual process simulation was conducted using Aspen HYSYS, with energy consumption and carbon emission analysis using Aspen Energy Analyzer. Process modifications included a new separation system incorporating a flash drum separator, liquid-liquid extraction, and reboiled absorber to achieve more high yield from 71796.84 kg/h to 71859.39 kg/h and purity from 94% to 99.05% and. The results showed improved efficiency purity and yield with reduced carbon emissions from 67680 kg/h to 14170 kg/h, with the potential for industrial sustainability through feedstock optimization and reduced environmental impact.

Keywords: 1,2-Ethylenedichloride; Carbon Emission; High Purity; Yield Maximizing

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1. Introduction

1,2-ethylenedichloride ($C_2H_4Cl_2$) is a chemical compound that has various industrial uses. The world demand for EDC since 1975 has increased by 5% per year. Therefore, it is estimated that in the next 18 years, EDC demand will reach 137,771,329 tons [1]. About 85% of the total ethylene dichloride production is used to produce vinyl chloride which is the main ingredient in the production of polyvinyl chloride (PVC), a multipurpose plastic used in various applications. In addition, about 10% of ethylene dichloride is also used in the production of chlorinated solvents such as 1,1,1-trichloroethane and tri- and tetrachloroethylene [2]. The remainder is used in various processes, mainly for the synthesis of ethylenediamine [3]. By reviewing the production of ethylene dichloride, innovation in the design of ethylene dichloride plants while taking into account certain aspects such as mass efficiency and total carbon emission efficiency.

The two main methods for ethylene dichloride (EDC) production are direct chlorination and oxychlorination. Direct chlorination, which reacts ethylene with chlorine, offers higher conversion efficiency and easier process control, making it more cost-effective and less energy-intensive [3]. However, this process requires pure chlorine, which can pose safety and handling issues. In contrast, oxychlorination, which uses ethylene, hydrogen chloride (HCl), and oxygen or air, is advantageous in recycling HCl,

* Corresponding Author.
Email: msyauqifinardhysaputr@students.undip.ac.id
(M.S.F. Saputra)

making it suitable for integrated operations that produce chlorine as a by-product [4]. While this method is more environmentally friendly because it recycles HCl, it also requires more complex reactions, higher energy usage, and increased risks associated with inside oxygen and heat management.

Ethylene dichloride (EDC) purification is critical to ensuring the quality and efficiency of downstream processes. High-purity EDC reduces operational disruptions, extends the service life of industrial equipment, and ensures compliance with product quality standards [5]. Impurities in EDC, such as water, organic chlorides, and other by-products, can cause catalyst poisoning, equipment corrosion, and reduced product yield in subsequent reactions [6]. By enabling recycling of by-products and reducing emissions of harmful substances such as carbon emissions, an effective purification process also helps to reduce waste and environmental impact. As a result, EDC purification is essential for maintaining process efficiency and supporting responsible and sustainable industrial practices [7].

To improve the production of ethylene dichloride in terms of economics and good conversion, this study will examine the design for ethylene dichloride plant using HYSYS simulation. The research study shows that overcoming this problem can be done by implementing sustainable design procedures at various stages of the process. Optimizing conversion and minimizing carbon emissions by selecting purification methods are in line with key targets in the industrial sector [8]. The objective of this research is to develop a modified process for producing ethylene dichloride by direct chlorination and oxychlorination methods, aiming to achieve mass efficiency, set up a plant that follows environmentally friendly principles, and maximizing yield with high purity of ethylene dichlorination products.

2. Methods

The basic process model of ethylene dichloride production via direct chlorination and oxychlorination was designed using Aspen HYSYS, and the corresponding process flow sheet is depicted in Figures 1 and 2. This simulation model serves to predict the process response of the plant 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 mimic actual plant processes. Aspen HYSYS process simulation tool was used to design a conceptual simulation model for ethylene dichloride production, following industry standards [9]. Process information for ethylene dichloride was sourced from the literature.

The conceptual process simulation model was developed specifically for the production of ethylene dichloride through direct chlorination and oxychlorination. Furthermore, the Aspen Energy Analyzer tool was used to analyze the energy consumption and total carbon emissions in all plant processes [10]. Aspen HYSYS was used to minimize total carbon emissions, and a conversion study of ethylene dichloride production. Detailed simulation by incorporating measurement operations that reflect the real-time concept of the plant's industrial processes..

In this research, an iterative simulation method was used to investigate, study, and compare the basic and advanced processes for ethylene dichloride production. The iterative simulation method entails repeated iterations using the software to adjust process parameters and observe their impact on the simulation results. The process begins by building a simulation model using Aspen HYSYS, analyzing the results with Aspen Energy Analyzer, and iteratively modifying the process parameters until the desired performance or results are achieved. The process modification carried out in this study is to adjust the process parameters and tools using the principles of the iterative simulation method. Further explanation of the modifications made can be seen in the next chapter.

In addition, this study involves a comparison between the initial ethylene dichloride purity and the purity after modification. The mass of ethylene dichloride mass was obtained using Aspen HYSYS. Furthermore, the %Purity was calculated as the ratio between the mass of ethylene dichloride product (kg/h) and the total mass of product (kg/h). The calculation of %Purity is expressed in Equation (1) [11]:

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

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

3. Result and Discussion

3.1 Process Description Before Modification

In the ethylene dichloride (EDC) production process, the materials used as raw materials are chloride, ethane, water, and chloride acid. At the initial stage, the ethane stream is split into two, one stream will be reacted with chloride (Direct

Chlorination) and the other stream will be mixed with chloride acid and water (Oxychlorination). Ethane and chloride will be reacted (Direct Chlorination) which begins with mixing in a mixer (MIX-100) with a pressure of 1.5 atm at a temperature of 25 °C. The mixture is flowed to the heater (E-100) to be heated to a temperature of 60 °C before being inserted into the reactor. The heater output temperature is adjusted using a controller (SET-1) so that the reactor output temperature is 60 °C. The reactor used is a stirred tank reactor (CSTR) with kinetic reaction. On the other hand, the other ethane stream will be reacted with air and chloride acid (Oxychlorination) in a flow pipe reactor (PFR). Ethane, air, and hydrochloric acid are mixed in a mixer (MIX-101) at 25 °C and 1.5 atm pressure. After that, the mixture is flowed to the compressor (K-100) until the pressure becomes 4 atm and the temperature increases to 137 °C. Before entering the PFR reactor, the mixture is passed through a heater (E-101) to increase the temperature to 225 °C. The outputs of the CSTR and PFR reactors are mixed using a mixer (M-102). Furthermore, it is cooled using a cooler with an output temperature of 15 °C. Next, the flash drum separator produces vapor product and liquid product. Liquid product is then put into three-phase distillation and will produce nitrogen, water, and ethylene dichloride. Also, heavy product is produced [12]. The simulation before modification can be seen at Figure 1 and Figure 2.

3.2 Properties and Reaction During Process

The physical properties of the compounds involved, such as boiling point, vapor pressure, density, and solubility, are very important in the ethylene dichloride (EDC) formation reaction (Table 1). Understanding these characteristics helps to control the reaction, separate the products, and implement safety procedures throughout the process [13].

Aside from the importance of understanding the physical properties of the compounds involved, reviewing the enthalpy of formation in ethylene dichloride (EDC) production reactions is crucial to understanding the energy requirements and thermodynamic efficiency of the process by knowing the nature of the reaction (endothermic or exothermic) [15]. Knowing the nature of the reaction can help determine the amount of energy required from outside, regulate the temperature, and make the right reactor design to achieve.

Chemical reaction of direct chlorination (DC) and oxychlorination (OX) [12], calculation of kinetic reaction [17] and calculation of ΔH reaction [18]:

$$C_2H_{(4)\,((g))} + Cl_{(2)\,((g))} \rightarrow C_2H_4Cl_{(2)\,((l))}$$

$$-r_1 = k_1 [C_2H_4] [Cl_{(2)}]$$

$$k_1 = 11493 \exp(-2156.8/T)\ m^3.mol^{-1}.s^{-1}$$

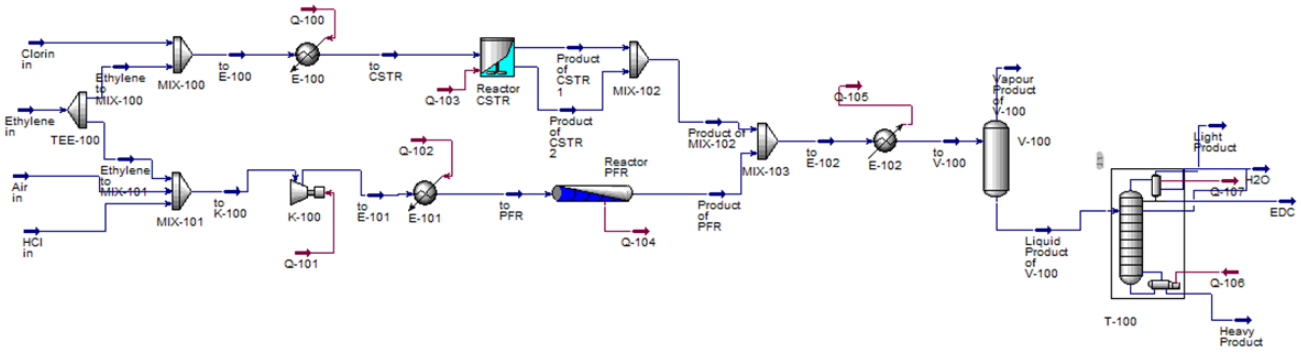

Figure 1. Basic process flow diagram of EDC production using Aspen HYSYS

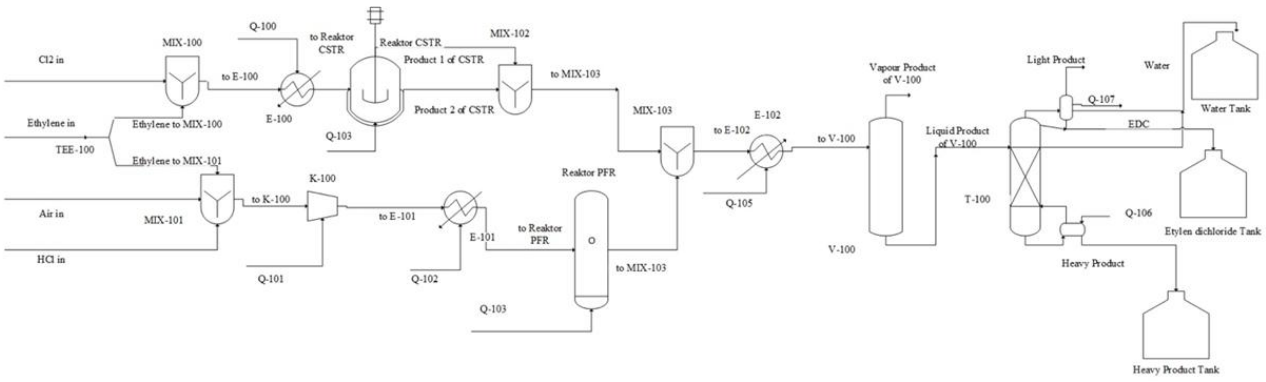

Figure 2. Process flow diagram of basic process of EDC production

$\Delta H_{dc} = \Delta H_{Product} - \Delta H_{Reactant}$
$\Delta H_{dc} = \Delta H_{C_2H_4Cl_2} - \Delta H_{C_2H_4} + \Delta H_{Cl_2}$
$\Delta H_{dc} = -129.7 - (52.30 + 0)$
$\Delta H_{dc} = -182$ kJ/mol
$\Delta H_{dc} = -182000$ J/mol

$$C_2H_{(4)\,((g))} + 2HCl_{\,(g)} + \frac{1}{2}O_{(2)\,((g))} \longrightarrow C_{(2)}H_4Cl_{(2)\,((l))}$$

$$-r_2 = \frac{269\,K_a[C_2H_4][Cl_2]\exp[-37800\ RT]}{1 + k_2[C_2H_4]}$$

$$-r_2 = \frac{168284\,[C_2H_4][Cl_2]\exp[-37800\ RT]}{1 + 630[C_2H_4]}$$

$\Delta H_{ox} = \Delta H_{Product} - \Delta H_{Reactant}$
$\Delta H_{ox} = \Delta H_{C_2H_4Cl_2} - \Delta H_{C_2H_4} + \Delta H_{HCl} + \Delta H_{O_2}$
$\Delta H_{ox} = -129.7 - (52.30 - 92.3 + \frac{1}{2}0)$
$\Delta H_{ox} = -239.2$ kJ/mol
$\Delta H_{ox} = -239200$ J/mol

Based on the calculation of the direct chlorination and oxychlorination enthalpy (ΔH) at a temperature of 298 K, the result shows a negative ΔH value. Therefore, it can be concluded that the ongoing reaction is an exothermic reaction that releases heat [19]. The ΔG_f data for each component at a temperature of 298 K can be seen in Table 2 [18].

Calculation of ΔG_f reaction for direct chlorination (dc):
$\Delta G_{f\,(dc)} = \Delta G_{f\,(Product)} - \Delta G_{f\,(Reactant)}$
$\Delta G_{f\,(dc)} = \Delta G_{f\,(C_2H_4Cl_2)} - (\Delta G_{f\,(C_2H_4)} + \Delta G_{f\,(Cl_2)})$
$\Delta G_{f\,(dc)} = \Delta G_{f\,(C_2H_4Cl_2)} - (\Delta G_{f\,(C_2H_4)} + \Delta G_{f\,(Cl_2)})$
$\Delta G_{f\,(dc)} = -73.85 - (68.12 + 0)$
$\Delta G_{f\,(dc)} = -141.97$ kJ/mol
$\Delta G_{f\,(dc)} = -141970$ J/mol
$\Delta G_{f\,298} = -R\ T \ln K_{298}$

Table 1. Physical properties of the main components [14]

Name	Ethylee	Chlorine	HCL	EDC	Unit
Molecular Formula	C_2H_4	CL_2	HCl	$C_2H_4Cl_2$	-
Molecular Weight	28.05	70.906	36.46	98.96	kg/kmol
Nomal boiling point	-103.8	-34.5	-85.1	83.4	°C
Critical temperature	282.4	417	324.6	561	K
Critical pressure	50.4	77	83.1	57.3	Bar
Critical volume	129	124	81	220	cm^3/mol
Liquid density	577 (-110)	1563 (-34)	1193 (-85)	1250 (16)	kg/m3 (°C)
ΔH_{vap} at nbp	13.553	20.432	16.161	32.029	kJ/mol
Explosion limit in air	2-36	-	-	6-16	%

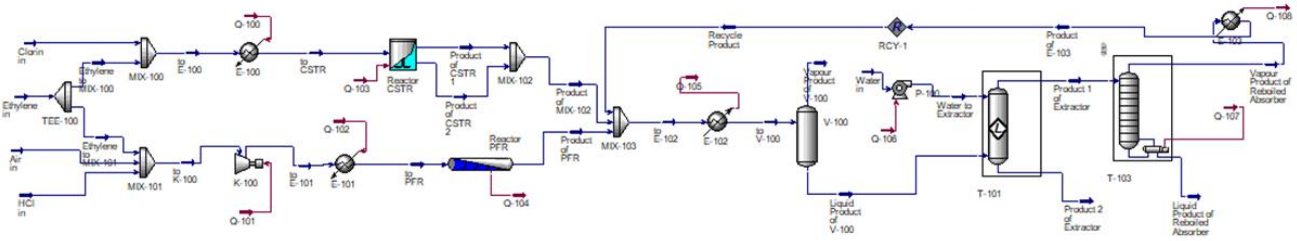

Figure 3. Modified process flow diagram of EDC production using Aspen HYSYS

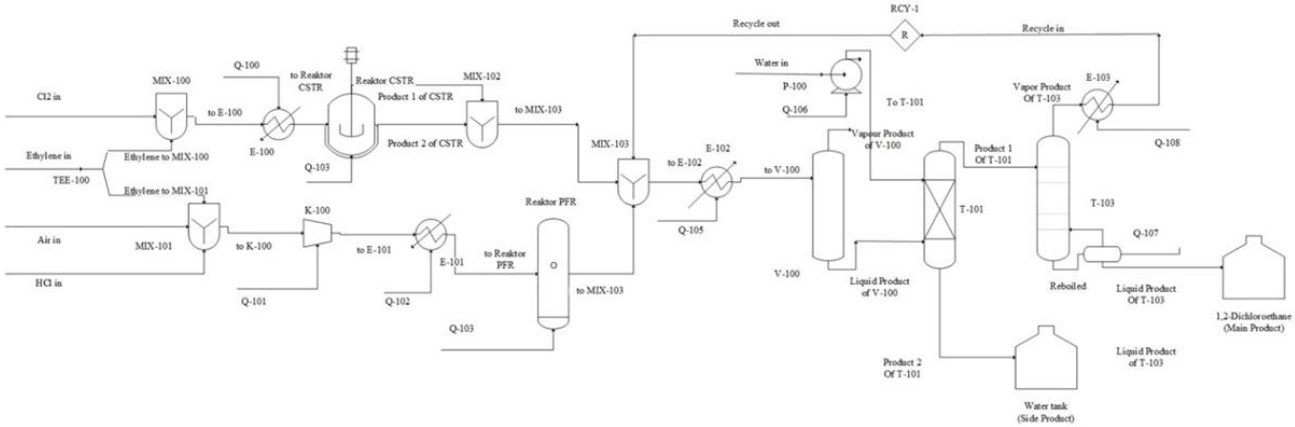

Figure 4. Figure 4. Flow diagram of modified process of EDC production

$$\ln K_{298} = \frac{\Delta G_{f\,298}}{-R\,T}$$

$$\ln K_{298} = \frac{-141970\ \frac{J}{mol}}{-\left(8.314\ \frac{J}{mol.\ K}\right)(298\ K)}$$

$$\ln K_{298} = 57.3020$$

$$K_{298} = 7.6908 \times 10^{24}$$

At operating temperature of 60 ºC (333 K):

$$\ln \frac{K_T}{K_{298}} = -\frac{\Delta H_{f\,298}}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right)$$

$$\ln \frac{K_{333}}{K_{298}} = -\frac{-182000\ \frac{J}{mol}}{8.314\ \frac{J}{mol.\ K}}\left(\frac{1}{333\ K} - \frac{1}{298\ K}\right)$$

$$\ln \frac{K_{333}}{7.6908 \times 10^{24}} = 57.3020$$

$$K_{358} = 3.4105 \times 10^{19}$$

Because of the value of $K_{333} > 1$, thus, the reaction of direct chlorination is irreversible [20]. The ΔG_f value of each component can be seen from Table 2. Calculation of ΔG_f reaction for oxychlorination (ox):

$$\Delta G_{f\,(ox)} = \Delta G_{f\,(Product)} - \Delta G_{f\,(Reactant)}$$

$$\Delta G_{f\,(ox)} = \Delta G_{f\,(C_2H_4Cl_2)} - (\Delta G_{f\,(C_2H_4)} + \Delta G_{f\,(HCl)} + \Delta H_{f\,(O_2)})$$

$$\Delta G_{f\,(ox)} = -73.85 - (-(68.12 - 95.3 + \frac{1}{2}0)$$

$$\Delta G_{f\,(ox)} = -179.97\ kJ/mol$$

$$\Delta G_{f\,(ox)} = -179970\ J/mol$$

$$\Delta G_{f\,298} = -R\,T \ln K_{298}$$

$$\ln K_{298} = \frac{\Delta G_{f\,298}}{-R\,T}$$

$$\ln K_{298} = \frac{-179970\ \frac{J}{mol}}{-\left(8.314\ \frac{J}{mol.\ K}\right)(298\ K)}$$

$$\ln K_{298} = 72.6397$$

$$K_{298} = 3.5238 \times 10^{31}$$

At operating temperature of 225 ºC (498 K):

$$\ln \frac{K_T}{K_{298}} = -\frac{\Delta H_{f\,298}}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right)$$

$$\ln \frac{K_{498}}{K_{298}} = -\frac{-239200\ \frac{J}{mol}}{8.314\ \frac{J}{mol.\ K}}\left(\frac{1}{498\ K} - \frac{1}{298\ K}\right)$$

$$\ln \frac{K_{498}}{7.6908 \times 10^{24}} = -38.7735$$

$$K_{498} = 5.1035 \times 10^{14}$$

Because of the value of $K_{498} > 1$, thus, the reaction of direct chlorination is irreversible [20].

3.3 Process Modification

The simulation process after modification can be seen from Figure 3 or Figure 4. for the result can be seen in Table 1 or Table S1 (Supporting Information). After the modification of the ethylene dichloride (EDC) formation process, cooling is carried out using a cooler that cools the output material from the process before modification which has a pre-cooled temperature of 71.8 °C to 15 °C. This process releases 48,030,000 kJ/h of heat energy. After being cooled by the cooler, separation is carried out, the separation system tool used by using three separators, namely the separator, liquid-liquid extractor, and reboiled absorber.

The waste treatment using separation system shown in the figure above includes the use of a flash drum separator (V-100), liquid-liquid extractor (T-101), and reboiled absorber (T-103). The flash drum separator functions to separate the gas and liquid mixture by utilizing the phase difference, which will produce vapour product and liquid product from the flash drum [21]. The liquid that comes out of the separator is then sent to the advanced process in the liquid-liquid extractor.

Liquid-liquid extractor (T-101) is used to separate liquid mixtures based on differences in solubility in certain solvents [22]. In this process, water is used to assist the separation of components, the water used is 100 kgmol/h with an initial temperature of 15 °C and a pressure of 1 atm and pumped to produce a pressure of 4 atm and a temperature of 15.02 °C which will be inserted into the liquid-liquid extractor. The result is two products, Product 1 of Extractor, which is a liquid with components that are more soluble in the solvent, and Product 2 of Extractor, a liquid with insoluble components. These products are separated based on the dissolved liquid phase.

The reboiled absorber (T-103) then separates the gas and liquid components further using the absorption principle assisted by reboiling. The liquid containing heavy components is separated at the bottom as Liquid Product of Reboiled Absorber, while the lighter components, in the form of gas, are removed as Vapor Product of

Table 2. Data of ΔG_f for each component at temperature 298 K

Component Name	Molecular Formula	$G_{f\,298\,K}$ (kJ/mol)
Ethylene	C_2H_4	68.12
Chlorine	Cl_2	0
Hydrochloric Acid	HCl	-95.3
Oxygen	O_2	0
Water	H_2O	-228.6
Ethylene Dichloride	$C_2H_4Cl_2$	-73.85

Reboiled Absorber. The system as a whole is designed to improve the separation efficiency of multicomponent mixtures in the process industry [23].

In this separation system, the output product from the reboiled absorber (T-103) consisting of liquid product and vapor product will undergo further processing before being recycled. The vapor product from T-103 will be cooled from 126.6 °C to 60 °C using a cooler (E-103) to reduce its temperature so that it is ready for use or further processing. After cooling, this product is flowed to the recycle system, which is then returned to the mixer (MIX-103).

At the mixer (MIX-103), the recycle product stream joins the new feed from the main process. This mixture is then cooled in the cooler (E-102) before entering the separator flash drum (V-100). The process is designed to improve separation efficiency and ensure the reuse of valuable components, while reducing waste and operating costs. With this recycle system, the separation process becomes more economical and sustainable as it maximizes the utilization of materials that have not been fully separated in the previous cycle. This process will continue to repeat, starting from separation in the flash drum, extraction in T-101, to absorption in T-103, resulting in an efficient and optimized separation cycle.

3.4 Emission of Carbon Analysis of Separation Operating System

Carbon emission analysis is carried out by varying the separator, which initially before modification uses a flash drum separator and three-phase distillation, while after modification uses a flash drum separator, liquid-liquid extraction, and reboiled absorber. This is done with the aim of minimizing the occurrence of carbon emissions by using the Case Study tool. The case study was conducted by changing the type of separation device. Figure 5 presents a comparison of carbon emissions using the system before modification with the system after modification.

The results of the case study show that the process before modification produces greater carbon emissions than those produced by the process after modification. The resulting process before modification produces carbon emissions of 67680 kg/h of carbon emissions. This amount is more than the process after modification which only produces carbon emissions of 14170 kg/h carbon emissions. The results of the modification process can produce products that have higher purity and produce smaller carbon emissions, this can be seen at Figure 5 and Table 3.

The post-modification process produces less carbon emissions than the pre-modification process due to improved flow circulation and

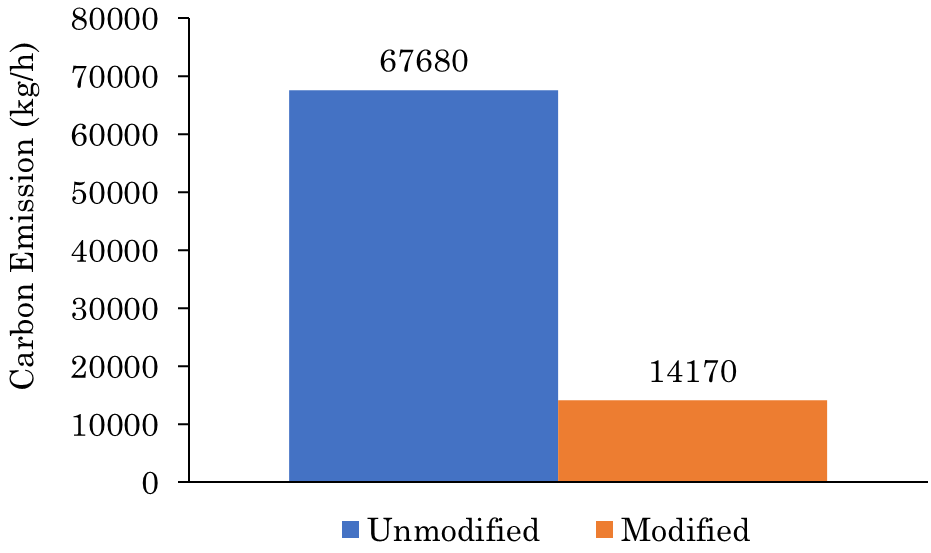

Figure 5. Comparison of carbon emissions

Table 3. Comparison basic process and modified process

Process	12-ethylene dichloride yield (kg/h)	12-ethylene dichloride purity (%)
Basic	71796.8362	94
Modified	71859.3916	99.05

integration of process units, such as the addition of separation and product recycling equipment in the first figure. This process allows more unreacted or excess by-products to be recycled into the system, thereby reducing raw material wastage and flue gas emissions [24]. With the recycle stream (recycle), the amount of gas or waste directly released into the atmosphere is reduced, as substances such as unreacted chlorine and ethylene are returned to the reactor for reuse. In addition, product separation becomes more efficient, and the purification process runs more optimally, resulting in less carbon emissions in the form of residual gases, which were not captured in the original design [25].

4. Conclusion

Process modifications to the production of 1,2-Ethylene dichloride must be carried out to achieve increased mass efficiency and low carbon emissions. Carbon emissions. Through process modification, the plant can optimize raw use, reduce environmental impact, increase product high purity, and improve operational efficiency. Based on the implemented process modification of waste treatment method, there has been an increase in the yield of 12-ethylene dichloride produced from 71796.84 kg/h with 94% of purity to 71859.39 kg/h with 99.05% of purity and carbon emissions from 67680 kg/h to 14170 kg/h. Further research on the 1,2-Ethylene dichloride process is still needed. In particular, the analysis of carbon emissions to develop the 12-Ethylene dichloride process to be more environmentally friendly in the use of raw materials. This is because analyzing its impact on the environment is very important, considering that in this decade, the world is experiencing the same starting to take environmental issues seriously. Pollution due to production is certainly a serious problem that is currently regulated and regulated.

CRediT Author Statement

Author Contribution: M.S.F. Saputra: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing, Review and Editing, and Supervision; R.F. Azhar: Conceptualization, Methodology, Formal Analysis, Data Curation, Writting Draft Preparation, Visualization, Software, Project Administration; T. Ramadhani: Validation, Writing, Review and Editing, Data Curation; V. Dodi: Investigation, Resource, Writing, Review and Editing. All authors have read and agreed to the published version of the manuscript.

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