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Research Article

Enhancing the Yield and Mass Production of Vinyl Chloride Production from Ethylene and Chloride through EDC Vapor Recovery in Direct Chlorination Process

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Abstract

Vinyl chloride (C_2H_3Cl) is produced using ethylene (C_2H_4) and chlorine (Cl) as primary raw materials. In Indonesia, the demand for raw materials to produce plastics, especially PVC, continues to grow each year. The chosen method is the direct chlorination of ethylene, resulting in the production of 1,2-dichloroethane (EDC). The process involves two conversion reactors, the CRV-100 and CRV-101. The CRV-100 reactor produces EDC vapor and some EDC compounds. However, these compounds are often not recovered and are released into the atmosphere. To increase efficiency and yield the process by recycling maximize the reactants, the EDC feedstock is replenished by recycling the top product from the CRV-100 reactor. After cooling and separation, liquid EDC is recovered and reintroduced, increasing vinyl chloride production, resulting the purity has increased from 93.93% to 97.14%, the total mass production rises from 2232.8919 kg/h to 5477.0938 kg/h before optimization, representing a 145.29% yield, reflecting a significant improvement in production efficiency.

Keywords: Vinyl Chloride; EDC Vapor Recovery; Chlorination; Methyl Chloride; 1,2-dichloroethane

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1. Introduction

The design and analysis of chemical processes are crucial subjects in chemical engineering education. For most processes, which are often complex, the design or analysis involves solving nonlinear equations. While manual calculation is an option, modern teaching methods now prioritize the use of computerized process simulators. One such tool is Aspen, is commonly used to simulate chemical processes in industries, including the production of vinyl chloride [1]. Vinyl chloride is a hazardous organic compound that plays a key role in producing polyvinyl chloride (PVC), a widely used plastic material [2]. In Indonesia, the demand for raw materials to produce plastics, especially PVC, continues to grow each year, as evidenced by consistently increasing data trends [3].

Vinyl chloride (VCM), represented by the molecular formula C_2H_3Cl, is a gaseous organic compound with a molecular weight of 62.5 g/mol. It plays a crucial role in the chemical industry as a versatile material with a wide range of applications. VCM is a major component in the production of copolymer resins, which have broad applications in various industries [4,5].

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In the previous research, a metal-free N-doped carbon was used as an efficient bifunctional catalyst of ethylene oxychlorination and EDC dehydrochlorination for the synthesis of VCM and EDC at low temperatures. However, the yield production is only up to 76% [6]. In the precious research, acetylene hydrochlorination and 1,2-dicholoroethane pyrolysis were used for manufacturing vinyl chloride. However, the result shows that the inert was increased and lack of molecular functionality [7].

The process of vapor recovery is an important policy in reaction engineering design. Vapor recovery system especially in the Vinyl Chloride production process not only aims resource utilization, but also the operational efficiency [8–10]. In this case, the innovation that proposed is by recycling maximize the reactants, the EDC feedstock is replenished by recycling the top product from the CRV-100 reactor (EDC vapor), which contains significant EDC. After cooling and separation, liquid EDC is recovered and reintroduced, increasing vinyl chloride production. This modification improves the yield and mass production of the Vinyl Chloride process [11]. The aim of this research is to improve yield and mass production of the vinyl chloride through EDC vapor recovery in direct chlorination process by simulating using Aspen HYSYS.

2. Methods

The production of vinyl chloride (C_2H_3Cl) is based on the use of ethylene (C_2H_4) and chlorine (Cl) as raw materials (Figure 1). The direct chlorination of ethylene is the selected method to produce 1,1-dichloroethane (EDC). The vinyl chloride manufacturing process involves two reactors, the CRV-100 and CRV-101 reactors.

In industrial operations, bubble column reactors are commonly used to circulate the reactants through the dispersion of EDC, which maximizes product output. Ethylene and chlorine, at 25 °C, 1.5 atm, and a molar flow of 90 kgmol/h, are introduced into the CRV-100 reactor, which operates at 65 °C and 1.5 atm. The chemical reaction in the CRV-100 reactor can be summarized by the following equation.

$$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g) \quad (1)$$

$$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g) + HCl(g) \quad (2)$$

Table 1. Standard entalphy of formation (ΔHf°298) for reaction components [13,14]

Component	$\Delta H°_{298}$ (kJ/mol)
Ethylene Dichloride	−129.7
Vinyl Chloride	28.5
HCl	−92.307

In the CRV-100 reactor, 95% of ethylene is converted in reaction 1, and 5% is converted in reaction 2. The primary product generated is 1,2-dichloroethane (EDC). The reactor output is then mixed with the recycle flow (RCY-1) in the MIX100 mixer. he resulting mixture is sent to the V-101 separator for separation. The liquid output is pumped by the P-100 pump and heated in the HE-100 heater to a temperature of 242 °C. This heated output is then directed into the CRV-101 reactor, which operates at 500 °C and 26 atm. The heat of reaction taking place in the CRV-101 reactor can be outlined as follows (Table 1):

$$C_2H_4Cl_2\ (g) \rightarrow C_2H_3Cl\ (g) + HCl\ (g) \quad (3)$$

$$\Delta H°_{298} = \Delta Hf°_{298\ (product)} - \Delta Hf°_{298\ (reactant)} \quad (4)$$

$$= (28.5 - 92.307) - (-129.7) = 65.893\ kJ/mol$$

The CRV-101 reactor achieves a 90% conversion of ethylene in reaction 3, with vinyl chloride being the primary product and HCl as the byproduct. The output of reactor is then cooled by cooler E-101, which reduces the temperature to 6 °C. The subsequent separation occurs in the T-100 distillation unit, where a shortcut column is utilized for this simulation. The relevant data for this process are outlined below.

The results of distillation unit at T-100 is obtained through the above shortcut column as outlined as follow: Stage number = 23; Feed Stage Location = 12; and Upper Product Expected is HCl 99.9%. The top result is mainly HCl, with a little amount of vinyl chloride, while the bottom result is primarily vinyl chloride, containing small amounts of HCl and EDC. The bottom product is then subjected to further separation in the T-101 distillation unit. Shortcut columns are used in this simulation, and the required data are presented in Table 3. The results of the T-101 distillation

Table 2. Shortcut column data of distillation column simulation (T-100)

Light Key in Bottom	HCl 0.1%
Heavy Key in Distilate	Vinyl chloride 0.1%
P Condensor	11.0 atm
P Reboiler	11.5 atm
Reflux Ratio (1.2 Rmin)	2.161

Table 3. Shortcut column data of distillation column simulation (T-101)

Light Key in Bottom	Vinyl Chloride 0.1%
Heavy Key in Destilate	EDC 0.1%
P Condensor	11.0 atm
P Reboiler	11.5 atm
Reflux Ratio (1,2 Rmin)	0.400

unit is obtained using the shortcut column as follows are as follow: Stage Number = 32; Feed Stage Location = 9, and Upper Product of Vinyl Chloride 0.1%.

The top result is vinyl chloride at 99.40%, while the bottom consists of 99.90% EDC. The bottom product is first cooled in cooler E-102 via valve VLV 100, bringing the temperature down to 65 °C. The EDC output from the cooler then undergoes a recycling process (RCY-1), and it is later mixed with EDC from the CRV-100 reactor using a MIX-100 mixer. his process will be carried out continuously and in sequence as long as the factory remains operational. The primary product generated is vinyl chloride (C_2H_3Cl), with HCl as a byproduct.

2.1 Direct Chlorination Design

The direct chlorination process is a leading method for manufacturing vinyl chloride from ethylene and chlorine. Firstly, ethylene and chlorine are combined in specific ratios and heated in a chlorination reactor. The core reaction takes place when ethylene reacts with chlorine, forming EDC as an intermediate. Following this, EDC undergoes dehydrochlorination, breaking down into vinyl chloride and hydrogen chloride [15]. Vinyl chloride can be separated from the reaction mixture and undergo further processing. The process demands tight control of operational conditions to secure high yields and quality and remains one of the most widely utilized methods in the chemical industry for producing vinyl chloride [16].

2.2 Purification of EDC

Once EDC is formed as an intermediate in the reaction between ethylene and chlorine, it is subjected to a separation and purification process to remove any impurities out-wanted substances [17]. This step is important for guaranteeing the quality of vinyl chloride, a key ingredient in the production of PVC. By purifying EDC, the process ensures that the final product meets quality standards, optimizing both the yield and efficiency of the overall production process [18].

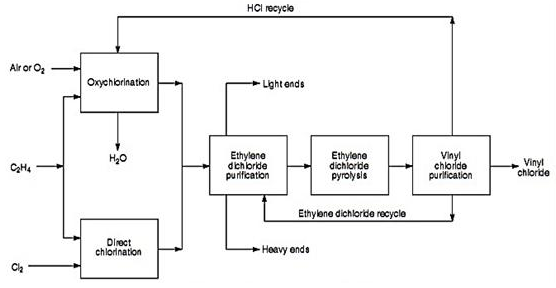

Figure 1. Basic block flow diagram in a balanced vinyl chloride process [12]

2.3 Purification of Vinyl Chloride

After vinyl chloride is formed in the reaction between ethylene and chlorine, the reaction mixture must pass through various verification and purification processes to remove any impurities or undesired compounds [19]. Distillation fractionation is used to separate vinyl chloride from other compounds produced during the chlorination reaction. Adsorption and chromatography can also be used to enhance the purity of vinyl chloride. This purification process is vital for ensuring the vinyl chloride meets the required industrial quality standards, which is crucial for the efficient production of polyvinyl chloride (PVC).

3. Result and Discussion

3.1 Thermodynamics Analysis

Reaction:

$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g)$ (1)

$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g)$ (2)

$C_2H_4Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g)$ (3)

At a temperature of 298 K, Reaction 1 (Table 4):

$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g)$

$\Delta G_{reaction} = \Delta Gf_{product} - \Delta Gf_{reactan}$ (5)

= 73.85 kJ/mol – (68.12+0) kJ/mol = 5.73 kJ/mol

$\Delta G_{reaction} = -RT \ln K$ (6)

$\ln K = -\frac{\Delta G reaction}{RT}$

$\ln K = -\frac{5.73\ kJ/mol}{8.314.10^{-3}\frac{kJ}{mol}.K^{298K}}$

$K = 0.099$

Reaction 2 (Table 4):

$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g)$ (2)

$\Delta G_{reaction} = \Delta Gf_{product} - \Delta Gf_{reactan}$

= (42.93 + (-95.3)) kJ/mol – (68.12+0) kJ/mol = -120.49 kJ/mol

$\Delta G reaction = -RT \ln K$

$\ln K = -\frac{\Delta G reaction}{RT}$

$\ln K = -\frac{-120.49\ kJ/mol}{8.314.10^{-3}\frac{kJ}{mol}.K^{298K}}$

$K = 13205 \times 10^{-16}$

Reaction 3:

$C_2H_4Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g)$

Table 4. The ΔG value of each component involved in reaction 1 and reaction 3 [14]

Component	ΔG_{f298} (kJ/mol)
C_2H_4	68.12
Cl_2	0
$C_2H_4Cl_2$	73.85
C_2H_3Cl	42.93
HCl	-95.3

$\Delta Gf_{reaction} = \Delta Gf_{product} - \Delta Gf_{reactan}$
= (42.93 + (-95.3)) kJ/mol – (73.85+0) kJ/mol = -126.22 kJ/mol
$\Delta G_{reaction} = -R\,T \ln K$
$\ln K = -\frac{\Delta Greaction}{RT}$
$\ln K = -\frac{-126.22\ kJ/mol}{8.314.10^{-3}\frac{kJ}{mol}.K^{298K}}$
$K = 1334\times10^{19}$

3.2 Basic Flowsheet (Block Flow Diagram)

The basic block flow diagram for producing vinyl chloride through the direct chlorination of ethylene and chlorine is illustrated in Figure 1. Over 90% of the total vinyl chloride produced is derived from a balanced process, with a simplified process flow diagram presented in Figure 2 [20], while the simulated by HYSYS is presented in Figure 3.

The plant design consists of three reactors and two separation units, which are responsible for purifying the intermediate products and the final vinyl chloride product. Ethylene is typically divided into nearly equal portions and fed into two chlorination units: direct chlorination and oxychlorination. In these units, reactions (1.3a) and (1.3b) take place, selectively producing EDC. Once purified, the EDC is vaporized and introduced into the furnace, where pyrolysis (reaction 1.3 c) occurs. After the cracking reactor, the process stream primarily consists of vinyl chloride, hydrogen chloride, and unreacted EDC, which is then directed to the VCM purification section. Here, almost pure hydrogen chloride and VCM are separated.

3.3 Process Modification by Increasing Yield and Mass Production of Vinyl Chloride

In the vinyl chloride production process, as illustrated in the process diagram (Figures 4 and 5), the composition of the output from the CRV-100 reactor (S1 Basic Flowsheet) contains a significant amount of EDC compounds. However,

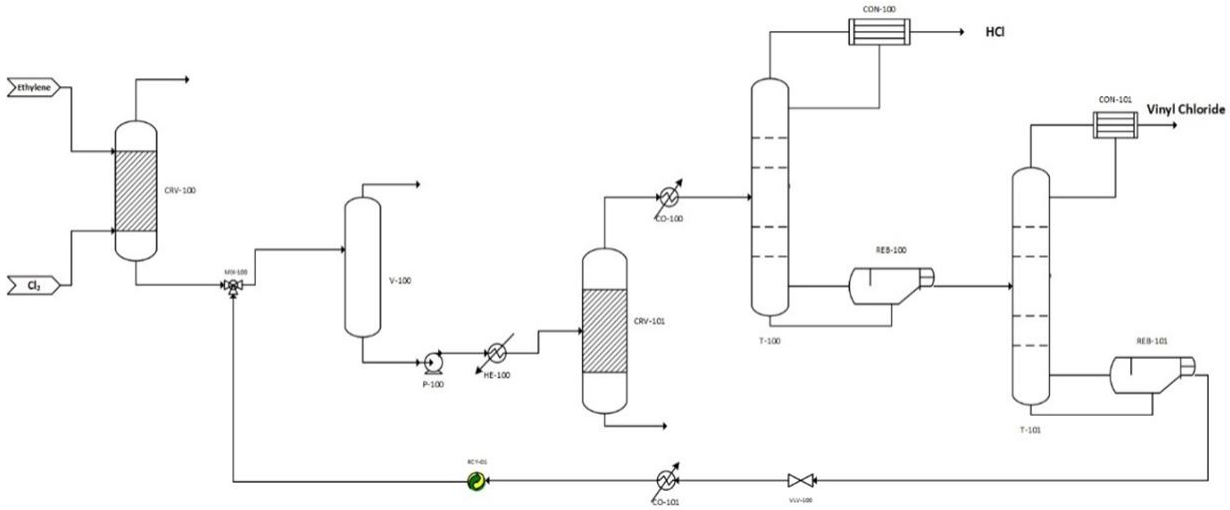

Figure 2. The basic block flow diagram for producing vinyl chloride through the direct chlorination of ethylene and chlorine [20]

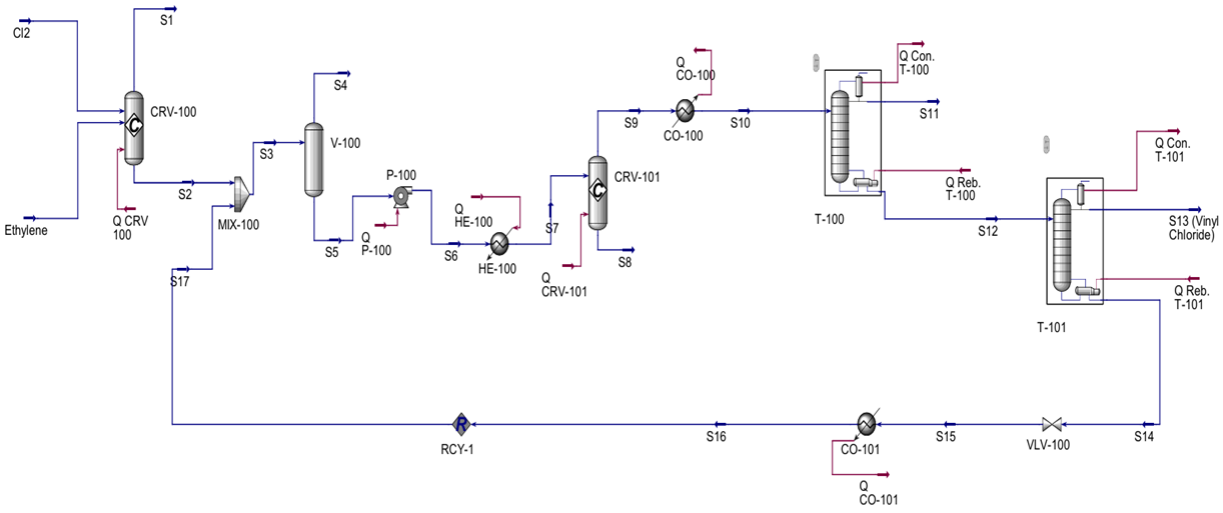

Figure 3. The simulation of unmodified process of vinyl chloride through the direct chlorination of ethylene and chlorine [20]

based on the literature and experimental data, these compounds are typically non-reusable and are directly released into the atmosphere. To enhance the efficiency of reactant usage, a process innovation can be implemented by directing the EDC Vapour through a cooler, where it is chilled to 10 °C under 1 atm pressure. As highlighted in Figures 4 and 5 and simulated mass and energy balance presented in Table S1 (Supporting Information), two primary recycle streams are present: the EDC is returned to its purification section, while hydrogen chloride is recovered through distillation and returned to the oxychlorination reactor. During steady-state operations, no fresh hydrogen chloride is added as the pyrolysis reactor provides all the hydrogen chloride needed for the oxychlorination process

This cooling step causes the EDC Vapour to condense from gas to liquid. The resulting EDC from the cooler still contains some gaseous components, which are separated using the Separator V-100. The liquid EDC (S-4) is then combined with liquid EDC from the CRV-100 reactor and EDC Recycle (S-22). In the same process, In the process, stream S-8 follows a similar methodology to the previous approach used for stream S-4. The EDC Vapour in stream S-8 is cooled to a temperature of 10°C under a pressure of 1 atm using a cooling unit. This step condenses the EDC Vapour, transitioning it from a gaseous to a liquid state. Subsequently, the condensed EDC is processed through a separator (V-103) to remove any residual gaseous components. The liquid EDC obtained (from stream S-10) is then reintegrated into the process stream to improve reactant utilization and reduce waste. The efficiency of the process and its contribution to increased mass production can be evaluated using the percentage yield (% yield), which measures the conversion of reactants into the desired product. It is calculated by dividing the moles of the actual product obtained by the theoretical moles of the product (the maximum possible amount if the entire limiting reagent is fully consumed in the reaction) [14].

The formula for calculating % yield is:

$$\text{Yield (\%)} = \frac{\text{mol of the product yielded}}{\text{mol of the product expected}} \times 100\% \qquad (7)$$

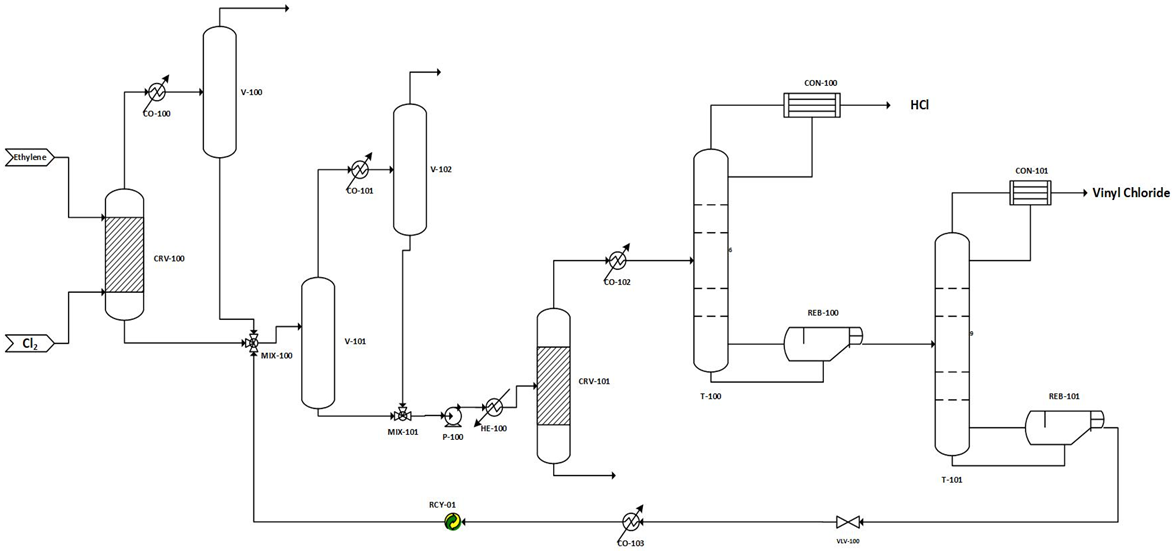

Figure 4. Modified process flow diagram of vinyl chloride production

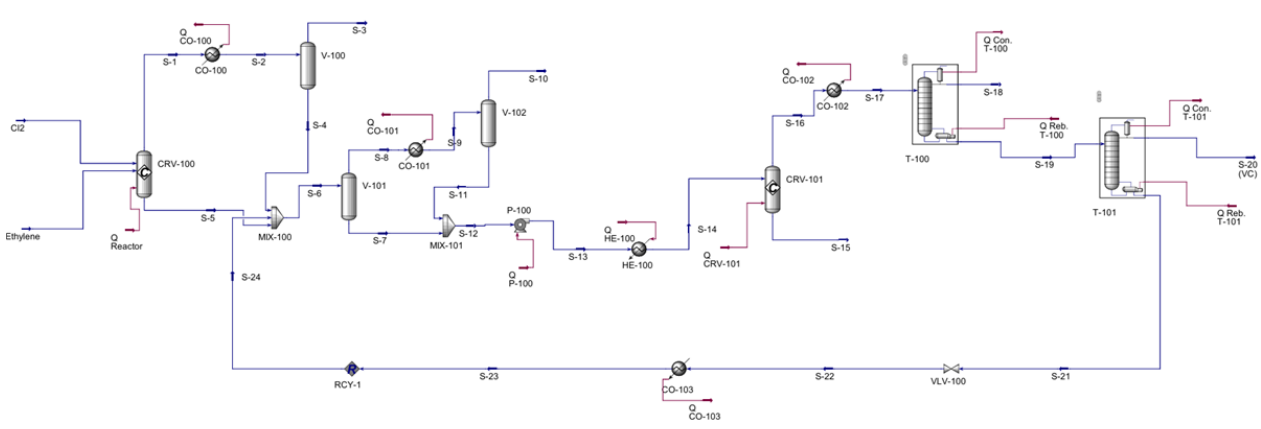

Figure 5. Modified process flow diagram HYSYS Simulation

4. Conclusions

By recycling the EDC vapor from the top product of the CRV-100 reactor, which contains a significant amount of EDC compounds, the EDC feedstock can be recovered and reused. The vapor is cooled and separated to obtain liquid EDC (EDC from SEP) via streams such as Stream S-4 and Stream S-8, which utilize similar methods. The EDC vapor in Stream S-8 is cooled to 10°C at 1 atm to condense it into a liquid, and the separated liquid EDC is reintroduced into the process stream. This optimization not only increases reactant utilization but also boosts the overall vinyl chloride production. As a result, the total mass production rises to 5477.0938 kg/h, compared to the initial 2232.8919 kg/h before optimization, representing a 145.29% yield improvement. Additionally, this process enhancement increases the annual production capacity of vinyl chloride to 48,000 tons per year, demonstrating the effectiveness of the implemented changes in improving efficiency, sustainability, and overall mass production. Furthermore, the yield has increased from 93.93% to 97.14%, reflecting a significant improvement in production efficiency.

CRedit Author Statement

Author Contributions: B.M. Aryaputra: Investigation, Resources, Software, Review and Editing, Supervision; A.N. Safitri: Conceptualization, Methodology, Review and Editing, Writing, Validation; D.K. Razita: Conceptualization, Review and Editing, Writing Draft Preparation, Visualization; S.H.P. Setyani: Methodology, Formal Analysis, Writing Draft Preparation, Review and Editing; A.Z. Mulfiana: Investigation, Data Curation, Writing. All authors have read and agreed to the published version of the manuscript.

References

[1] He, M., Chen, F., Wen, P., Jin, Y., Zhao, J., Zhang, L., et al. (2024) Vinyl Chloride Distillation Process Simulation Optimization Evaluation: Optimization Based on NSGA-III Algorithm and Quantitative Risk Analysis. *Processes*. 12(11), 2-21. DOI: 10.3390/pr12112413.

[2] Kudzin, M.H., Piwowarska, D., Festinger, N., Chruściel, J.J. (2023). Risks associated with the presence of polyvinyl chloride in the environment and methods for its disposal and utilization. Materials, 17 (1), 173. DOI: 10.3390/ma17010173.

[3] Lewandowski, K., Skórczewska. K. (2022) A Brief Review of Poly(Vinyl Chloride) (PVC) Recycling. *Polymers (Basel)*. 14(15), 3035. DOI: 10.3390/polym14153035

[4] Daniels, P.H. (2009) A brief overview of theories of PVC plasticization and methods used to evaluate PVC-plasticizer interaction. *J. Vinyl Addit. Technol.* 15(4), 219–223. DOI: 10.1002/vnl.20211

[5] Carroll, W.F., Johnson, R.W., Moore, S.S., Paradis, R.A. (2011) Poly(Vinyl Chloride) . *Applied Plastics Engineering Handbook*: Processing and Materials. Elsevier; 2011. 61–76 p. DOI: 10.1016/B978-1-4377-3514-7.10005-4

[6] Ma, H., Ma, G., Qi, Y., Wang, Y., Chen, Q., Rout, K.R., et al. (2020) Nitrogen-Doped Carbon-Assisted One-pot Tandem Reaction for Vinyl Chloride Production via Ethylene Oxychlorination. *Angew Chemie - Int Ed*. 59(49), 22080–22085. DOI: 10.1002/anie.202006729

[7] Andliyani, L., Alfandi, I., Inda, N., Putri, K. (2023). Production of Vinyl Chloride from Ethylene: Technology Review and Process Production of Vinyl Chloride from Ethylene: Technology Review and Process Selection. (September), 1–6. International Engineering Student Conference.

[8] Kim, D.M., Kim, Y.W., Cho, J. (2010) A comparative study on the recovery of 1,2-dichloroethane and the removal of benzene contained in the byproducts of VCM process. *Korean J. Chem. Eng.* 27(3), 970–976. DOI: 10.1007/s11814-010-0206-7

[9] Ardhiany, S.P. (2019) Proses absorbsi gas CO2 dalam biogas menggunakan alat absorber tipe packing dengan analisa pengaruh laju alir absorben naoh. *J. Tek. Patra Akad*. 9(02), 55–64. DOI: 10.52506/jtpa.v9i02.78

[10] Akintola, J., Patinvoh, R., Moradeyo, O., Akpan, J. (2024) Sustainability an integrated process route for the synthesis of vinyl chloride monomer. *RSC Sustainability*, 3(1), 526-539. DOI: 10.1039/D4SU00326H.

[11] Martinez V. (1999). United States Patent. 5,891,318.

[12] Kirk, R.E., Othmer, D.F., Grayson, M., Eckroth, D. (2004) Kirk-Othmer Encyclopedia of Chemical Technology, Wiley Vol. 5. 2003. p. 186–190.

[13] Smith, J.M. (1950) Introduction to chemical engineering thermodynamics. *Journal of Chemical Education*. Vol. 27. p. 584, DOI: 10.1021/ed027p584.3.

[14] Carl, L.Y. (2015) The Yaws Handbook of Vapor Pressure. The Yaws Handbook of Vapor Pressure. Gulf Professional

[15] Higham, M.D., Scharfe, M., Capdevila-Cortada, M., Pérez-Ramírez, J., López, N. (2017) Mechanism of ethylene oxychlorination over ruthenium oxide. *J. Catal.* 353, 171–180. DOI: 10.1016/j.jcat.2017.07.013

[16] Panjapornpon, C., Bardeeniz, S., Hussain, M.A. (2023) Deep learning approach for energy efficiency prediction with signal monitoring reliability for a vinyl chloride monomer process. *Reliab. Eng. Syst. Saf.* 231, 109008. DOI: 10.1016/j.ress.2022.109008

[17] Scharfe, M., Lira-Parada, P.A., Amrute, A.P., Mitchell, S., Pérez-Ramírez, J. (2016) Lanthanide compounds as catalysts for the one-step synthesis of vinyl chloride from ethylene. *J. Catal.*. 344, 524–34. DOI: 10.1016/j.jcat.2016.10.026

[18] Samiee, L., Goodarzvand-Chegini, F., Khalili-Garakani, A., Kargari, N., Rahmanian, N. (2023) Feasibility study of organochlorine waste processing and recycling in the vinyl chloride production unit: techno-economic assessment and emission estimation. *J. Mater. Cycles Waste Manag*. 25(6), 3530–3544. DOI: 10.1007/s10163-023-01776-8

[19] Mnyango, J.I., Hlangothi, S.P. (2024) Polyvinyl chloride applications along with methods for managing its end-of-life items: A review. *Prog. Rubber, Plast. Recycl. Technol. Recycling Technology*, 1–59. DOI: 10.1177/14777606241308652

[20] Rossanese, G. (2015). Modelling of an industrial plant for vinyl chloride production. *PhD Thesis*, Univ Degli Stud Di Padova

[21] Lee, T.A. (1995) Lab Notebooks. *Chem. Eng. News*. 73(36) 20.