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Research Article

Purity Enhancement of Vinyl Chloride Monomer from Ethylene Dichloride Using Distillation Column Optimization and Recycle Integration

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Abstract

Vinyl Chloride Monomer (VCM) is a key precursor in the manufacture of polyvinyl chloride (PVC), a polymer of considerable industrial significance. A major synthetic route to VCM involves the reaction of ethylene dichloride (EDC), producing VCM and hydrogen chloride as the principal products. This study aims to enhance the purity of VCM by implementing process improvements through the integration of distillation columns and recycling systems. The optimized configuration achieved an outstanding VCM purity of 99.97%, while simultaneously increasing energy efficiency and minimizing the formation of undesirable by-products. These results underscore the critical importance of advanced reactor design and purification technologies in elevating VCM quality, thereby contributing to more sustainable PVC production within the chemical industry.

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Keywords: Vinyl Chloride Monomer; Ethylene Dichloride; Thermal Cracking

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1. Introduction

The global demand for polyvinyl chloride (PVC) continues to rise, driven by its extensive applications in construction, packaging, and consumer products. Vinyl chloride monomer (VCM), the critical precursor for PVC, is primarily synthesized via the thermal cracking of ethylene dichloride (EDC), a process characterized by complex reaction pathways and substantial energy requirements [1]. In industrial practice, optimizing this process is essential to enhance yield, lower operational costs, and mitigate environmental impacts [2]. The principal reaction can be represented as [3]:

$$C_2H_4Cl_{2(g)} \rightarrow C_2H_3Cl_{(g)} + HCl_{(g)} \quad \Delta H_{298} = 62.85 \text{ kJ/mol} \quad (1)$$

where EDC decomposes into VCM and hydrogen chloride. Nevertheless, side reactions and coke deposition frequently diminish selectivity and product purity, underscoring the importance of process optimization to meet stringent industrial specifications [4].

To comply with stringent industrial specifications, particularly those requiring high-purity vinyl chloride monomer (VCM), systematic process optimization has been recognized as essential [5]. Conventional thermal cracking of ethylene dichloride (EDC) has been reported to yield VCM with purities typically ranging between 85–95%; however, achieving 99% purity necessitates targeted modifications to the process flow diagram (PFD) and operating conditions [2].

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Attaining such levels of purity remains challenging due to the need for precise regulation of reactor temperature, careful adjustment of residence time, and the incorporation of advanced separation systems capable of efficiently removing hydrogen chloride while recycling unreacted EDC [6]. These considerations highlight the critical role of integrated process design and optimization in advancing VCM production toward industrially viable, high-purity standards.

This study investigates the optimization of vinyl chloride monomer (VCM) synthesis from ethylene dichloride (EDC) via thermal cracking at an industrial scale capacity of 250,000 tons per year, employing Aspen HYSYS V.11 as the simulation platform (Figure 1). Process modifications were introduced to enhance product purity, including the optimization of reactor operating parameters, the integration of an additional distillation column and the design of a recycling system. Sensitivity analyses and optimization tools available within Aspen HYSYS were utilized to identify the most favourable operating conditions, thereby achieving 99.97% VCM purity. The optimized configuration demonstrated high conversion efficiency, improved selectivity, and sustainable energy integration, underscoring the potential of advanced process design in meeting stringent industrial requirements.

2. Method

To improve the purity of vinyl chloride monomer (VCM) and through modification of the adding column distillation and recycle the bottom product which is ethylene dichloride (EDC). The physical condition is liquid of compound is determined based on the vapor pressure equilibrium data of the pure compound, which is calculated using HYSYS software with 2 property packages, namely the NRTL (Non-Random Two-Liquid) model and the UNIQUAC model to determine the actual composition of each component [8]. NRTL (Non-Random Two-Liquid) is an activity model used in thermodynamics to predict the behavior of non-ideal mixtures, especially in liquid mixtures. This model serves to calculate the activity of components in the mixture. Activity is a parameter that indicates the extent to which a component in a liquid mixture approaches the behavior of the pure substance and its deviation from ideal conditions [9]. NRTL models are used in chemical process simulations to model the interactions between components in a mixture, predict the distribution of each component at various process points, and support overall process optimization. The phase equilibrium of non-ideal mixed systems is calculated using the NRTL Model. These calculations include the determination of dew point, freezing point, as well as various thermodynamic parameters required to analyze and design a process [8].

Our modification of vinyl chloride monomer production process is based on the existing literature. We modified the vinyl chloride monomer production process directly through the ethylene dichloride process with a capacity of 250,000 tons per year by adding a column distillation equipment at the end of the process so that there are three distillation columns in this vinyl chloride monomer production process. The purpose of adding a distillation column in this study is to increase the purity of the product we want, namely high purity vinyl chloride monomer. This is based on existing research, where the distillation process removes mixture of EDC, HCl, and other unwanted compounds that may form during the reaction, thus pushing the reaction equilibrium to the right to produce a purer product and ensure high reaction performance [10].

In this process, a mixer (M-100) is used to mix the materials with an output flow rate of 59957,3774 kg/h and a molar ratio of Ethylene Dichloride : VCM : HCl = 1 : 1 : 1. After being mixed in the mixer (M-100), the feed from the mixer output stream was then fed into the pump (P-100) followed by the heat exchanger for preheating, before finally entering the reactor. In

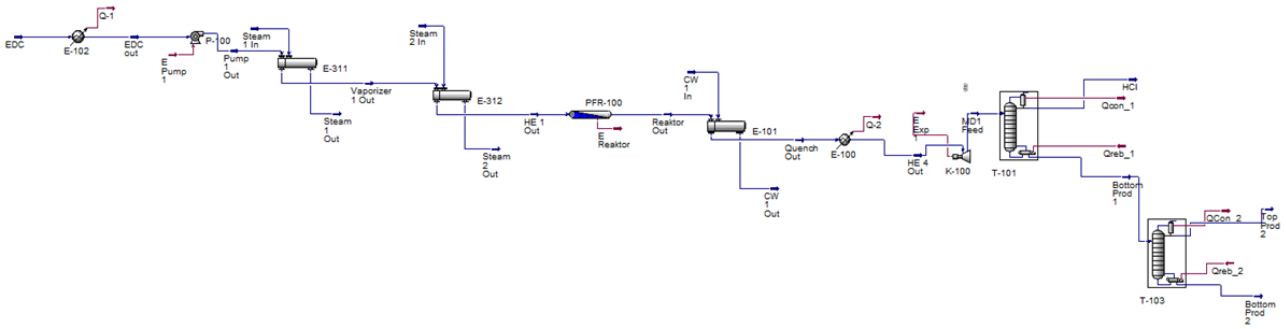

Figure 1. Simulation vinyl chloride monomer before modification with Aspen HYSYS [7].

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the Aspen HYSYS simulation, the reactor used for this process is a Plug Flow Reactor because the thermal cracking reaction is endothermic at high temperatures, making the tubular reactor more effective in maintaining the temperature profile and providing uniform heat transfer throughout the reactor. Furthermore, the PFR allows for controlled residence time and minimizes side reactions, resulting in higher conversions and lower coke formation [11]. The Plug Flow Reactor operates at a temperature of 500 K and a pressure of 1824 kPa.

The methodology described by Zhu [12], which is based on the relative volatility of the compounds used for the synthesis of the separation system. The reactor outlet is a two-phase stream, i.e. from the most volatile to the least volatile consisting of vinyl chloride monomer and ethylene dichloride. EDC is reagent can be recycled into the process, thus reducing feedstock expenditure. The reactor output enters the separator (T-101-3) to separate the mixture of vinyl chloride monomer and recycle EDC from the desired product, vinyl chloride monomer.

The reactor outlet from VCM synthesis is a two-phase stream containing vinyl chloride monomer (VCM) and ethylene dichloride (EDC). This stream is directed to a multi-stage separation sequence consisting of three distillation columns. The first column removes the most volatile fraction (VCM), while the intermediate column further purifies VCM by removing heavier components. The third column recovers EDC as a bottom product, which is then recycled to the mixer to reduce feed costs and improve process economics. Multi-column distillation systems have been demonstrated to provide higher product purity and better separation performance for complex mixtures with close relative volatility, as well as reduced energy consumption compared to single-column systems. Such multi-stage distillation sequences are widely reported in literature as necessary for effective multicomponent separations with stringent purity targets [13].

3. Results and Discussion

In this process, vinyl chloride monomer (VCM) is obtained through the thermal cracking of ethylene dichloride (EDC), yielding VCM and hydrogen chloride (HCl) as products. The chemical reaction can be represented in Equation (1). The VCM production process simulated in ASPEN HYSYS was enhanced by integrating a distillation unit and recycling the bottom stream, ethylene dichloride (EDC). The resulting modified flowsheet for VCM production is presented in Figure 2. Ethylene dichloride (EDC) is first pressurized and directed into a heat exchanger, where it undergoes phase transition from liquid to vapor. The vaporized EDC enters the Plug Flow Reactor (PFR) at an inlet temperature of 216 °C. Inside the reactor, EDC is thermally cracked to produce vinyl chloride monomer (VCM) and hydrogen chloride (HCl), with the reaction stream exiting at 500 °C. The effluent is subsequently cooled in a downstream heat exchanger to 134 °C. At this stage, the stream pressure is 658 kPa, which is further reduced to 506.6 kPa using an expander.

The separation of products and unreacted ethylene dichloride (EDC) is carried out through a three-stage distillation sequence. Each distillation unit produces a top and bottom stream. In the first distillation, the overhead stream contains 63.88% HCl, 36.03% VCM, and no EDC, while the bottom stream consists of 79.86% VCM and 20.13% EDC. This bottom stream is further processed in the second distillation, yielding an overhead composition of 75.21% VCM, 23.79% EDC, and 1% HCl. The bottom stream from the second distillation, comprising 25.81% VCM and 74.19% EDC, is subsequently separated in the third distillation. The overhead product of the third distillation achieves high purity, with 99.97% VCM, 0.03% EDC, and no HCl, while the bottom product consists of 99.99% EDC and 0.01% VCM. The bottom stream from the third distillation is recycled to the mixer, where the recovered EDC is

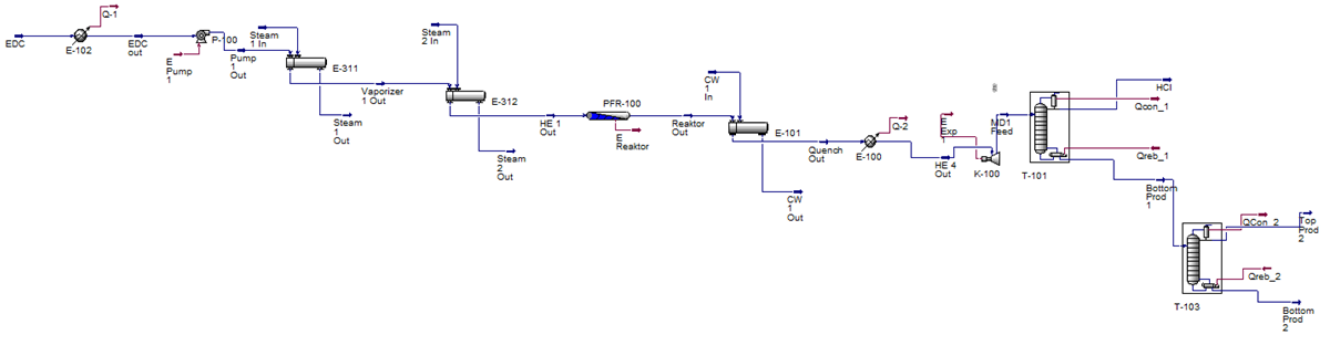

Figure 2. Simulation vinyl chloride monomer after modification using Aspen HYSYS [7].

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combined with fresh EDC feed for reintroduction into the reaction system.

Following the process modification, the purity of VCM increased markedly to 99.97%, representing a substantial improvement over the unmodified process, which achieved only 40.46%. The modification on basic Process Flow Diagram (PFD) (Figure 3) involved the addition of an extra distillation column to enhance component separation efficiency within the process stream (Figure 4). This additional unit provided increased vapor–liquid contact stages, thereby significantly improving separation selectivity. As a result, the new configuration enabled a sharper distinction between VCM and residual impurities. The attainment of 99.97% purity clearly demonstrates that the incorporation of the distillation column enhanced purification efficiency and yielded a product of superior specification [14].

A recycle stream is integrated into the process to optimize feedstock utilization by stabilizing and adjusting the composition of the reactor feed. The presence of recycle enhances the effectiveness and uniformity of contact between the reactants, thereby increasing the probability of reaction during each flow cycle. As a result, the overall process conversion is improved, leading to a reduction in unreacted feedstock that would otherwise remain as impurities in the final product. This modification ultimately yields a product of higher purity [15].

This process modification is designed to improve the purity of VCM, as product purity directly governs its overall quality. Higher purity levels correspond to fewer impurities, thereby enhancing both the quality and performance of the final product [16]. To evaluate this improvement, the purity of the product must be calculated using mass flow data generated from Aspen HYSYS, followed by computation with the purity percentage formula. The mass flow rate data obtained prior to and after modification are presented in Table 1.

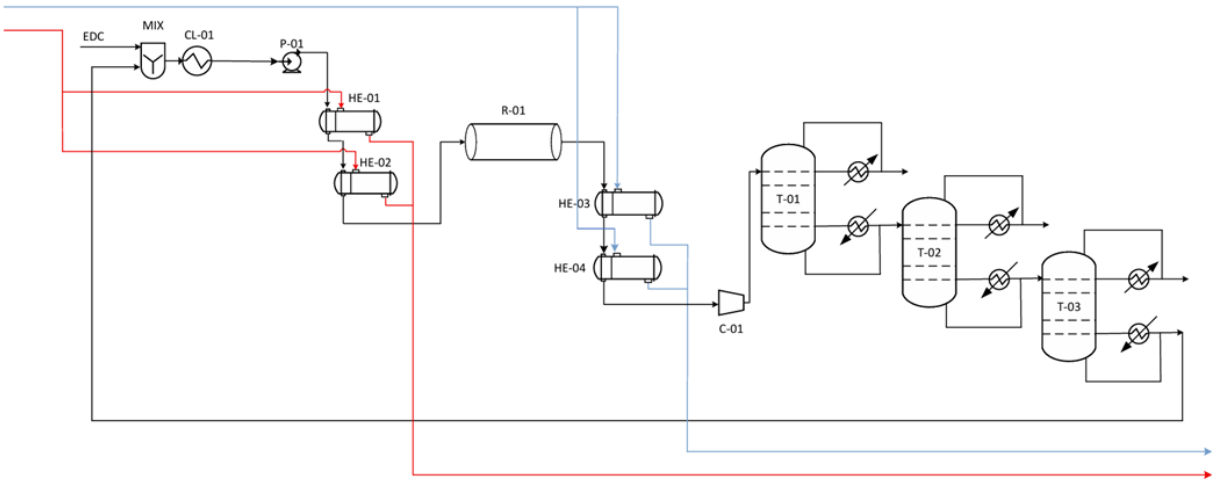

Figure 4. Process flow diagram of vinyl chloride monomer production after modification.

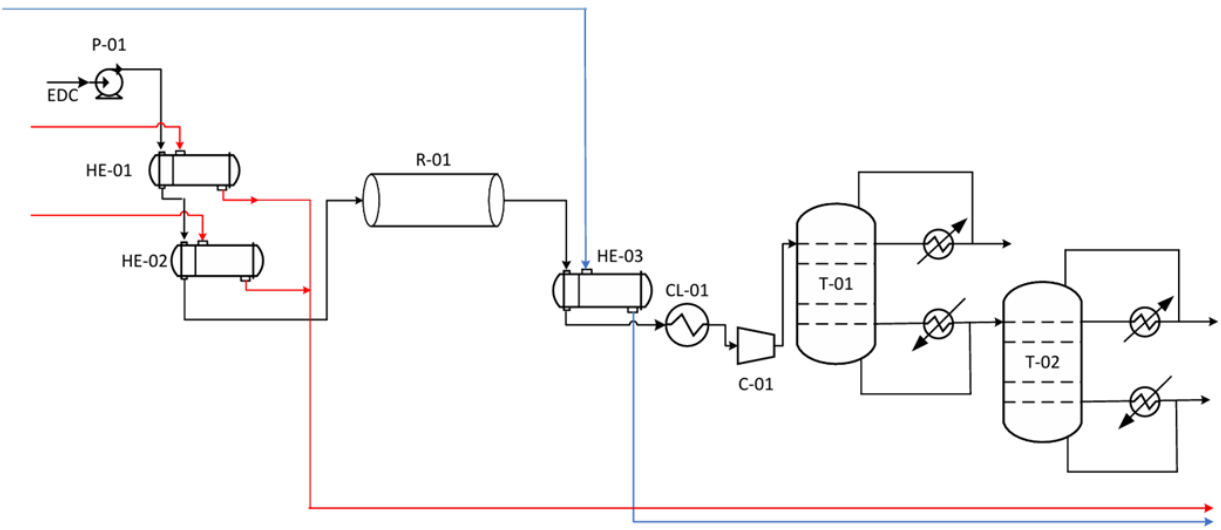

Figure 3. Process flow diagram of vinyl chloride monomer production before modification.

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Based on the data and calculation results, the product purity prior to process modification was determined to be 40.46% (%Purity = ((mole fraction of product)) / (total mole fraction) × 100% [17]. To assess the purity after the modification, a recalculation must be performed using the same formula to be 99.97%. A comparative summary of the process before and after modification is provided in the Table 2. As shown in Table 2, the modified process yielded a significantly higher VCM purity of 99.97%, compared to 40.46% in the unmodified process. Furthermore, the modified process required a reduced amount of EDC, at 40,077.4049 kg/h, relative to 49,984.8485 kg/h in the unmodified process.

4. Conclusion

The optimization of vinyl chloride monomer (VCM) production via thermal cracking of ethylene dichloride (EDC) has yielded substantial gains in both product purity and process efficiency. Incorporating an additional distillation column and a recycle loop for unreacted EDC elevated VCM purity dramatically, from 40.46% in the baseline process to 99.97% in the optimized configuration. Aspen HYSYS V.11 was employed to rigorously evaluate reactor performance, separation efficiency, and phase behavior using NRTL property models, ensuring precise thermodynamic representation of the non-ideal liquid systems. The adoption of a Plug Flow Reactor (PFR) under high temperature and controlled pressure conditions enhanced conversion rates while suppressing side reactions. Meanwhile, a three-stage distillation sequence achieved selective separation of VCM, HCl, and EDC with high efficiency. Recycling purified EDC back into the reactor feed further improved process economics and conversion effectiveness. Collectively, this integrated optimization, encompassing reactor parameter tuning, advanced separation design, and strategic recycling, demonstrates the critical role of systematic process enhancement and simulation-driven decision-making in achieving high-purity VCM production that meets stringent industrial standards.

CRedit Author Statement

Author Contributions: A.O.A Putri: Writing–review & editing, Writing–original draft, Resources, Methodology, Conceptualization, Investigation. M.P.T Dewi: Writing–review & editing, Writing–original draft, Resources, Methodology, Formal analysis. N.A.I Sofyar: Writing–review & editing, Writing–original draft, Methodology, Formal analysis, Conceptualization, Validation Data curation; R.E Candraningtyas: Writing–review & editing, Methodology, Formal analysis, Conceptualization, Validation Data curation, Software (Aspen HYSYS simulation). S.N Zulfa: Writing–review & editing, Writing–original draft, Methodology, Resources, Software (Aspen HYSYS simulation). All authors have read and agreed to the published version of the manuscript.

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Table 1. Mass flow rate of unmodified process.

Before modification		After modification	
Component	Mass flow rate (kg/h)	Component	Mass flow rate (kg/h)
Vinyl Chloride Monomer	485.1380	Vinyl Chloride Monomer	0.2901
Ethylene dichloride	713.7290	Ethylene dichloride	0.0001
HCl	0.2704	HCl	0
Total Product	1199.1374	Total Product	0.2902

Table 2. Performance comparison of unmodified and modified processes.

Parameter	Unmodified Process	Modified Process
Number of Distillation Units	2	3
Recycle	No	Yes
Purity (%)	40.46	99.97
EDC *Feed Requirement*(kg/h)	49984.8485	40077.4049

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