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Research Article

Optimizing Net Energy Efficiency of Vinyl Chloride Monomer (VCM) Production by Modifying Heat Transfer Process

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Abstract

The acetylene hydrochlorination process is a highly exothermic reaction, causing the reactor temperature to rise, which then requires cooling through a heat exchanger. A modification of the process is necessary to enhance the heat efficiency of the acetylene hydrochlorination by utilizing the heat generated by the reactor. Heat transfer fluid serves as a medium for both heating and cooling, enabling a looping heat transfer process. The heat transfer fluid system absorbs heat from the reactor and subsequently reuses this heat to warm the reactor feed, eliminating the need for additional energy input. The process modification was modeled using Aspen HYSYS, and the heat efficiency between the basic and modified processes was compared using the net-energy formula. The results showed that the net-energy (NE) for the basic and modified processes were 38,811,930.515 kJ/h and 18,702.951 kJ/h, respectively. This indicates that the modified process offers better energy efficiency, as the net-energy value is closer to zero compared to basic process. Thus, this modification improves the heat efficiency of VCM production through the acetylene hydrochlorination process.

Keywords: VCM; Net energy; Hydrochlorination; Process modifications; Heat efficiency

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1. Introduction

Vinyl Chloride Monomer (VCM) is a colorless gas under standard room temperature conditions and serves as a crucial industrial chemical primarily utilized in the production of the Polymer Polyvinyl Chloride (PVC) [1]. PVC is a versatile polymer that serves as a raw material for various applications, with approximately 95% of VCM produced is directed towards PVC manufacturing, highlighting its significance in the plastics industry [2,3]. There are three primary industrial methods for producing VCM: ethylene oxychlorination, ethane pyrolysis, and acetylene hydrochlorination. Among these, acetylene hydrochlorination is more commonly used in regions abundant in coal resources [4]. Vinyl chloride monomer (VCM) plays a critical role in the production of polyvinyl chloride (PVC), with over 70% of PVC manufacturing in China relying on acetylene hydrochlorination. This is driven by the country's abundant coal resources and the rising prices of petroleum. Alongside ethylene and sodium hydroxide, vinyl chloride is one of the world's most significant commodity chemicals. Its importance stems from the extensive applications of polyvinyl chloride, which ranks among the most widely used polymers globally [5].

In 2013, global polyvinyl chloride (PVC) production reached approximately 61 million tons, with China accounting for over half of this total at 38.5 million tons. By 2025, PVC production is projected to rise to 63.7 million tons, while demand is expected to reach 51.6 million tons [6]. The primary PVC producers are located in Asia (48%)

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and North America (13%). Asia also leads in consumption, accounting for 58% of the global total, while Europe contributes 17% [7]. The catalytic hydrochlorination of acetylene can occur in either the gas phase or the liquid phase, with the gas-phase reaction being the preferred method in industrial applications. In this process, gaseous reactants are exposed to a catalyst under moderately elevated pressures (0.1–0.3 MPa) and temperatures ranging from 100–250 °C, with a contact time of 0.1–1 second. Acetylene conversions of 95–100% with nearly quantitative yields can be achieved (Figure 2) [8].

Mercury(II) chloride on activated carbon is primarily used as a catalyst at concentrations of 2–10 wt%. Several other metallic catalysts, as well as 1–3 vol% chlorine, have been suggested or patented. However, the mercury salt has been shown to be the most effective. The reaction rate is first order with respect to acetylene [9]. The reaction of hydrochlorination of acetylene is highly exothermic ($\Delta H = -124.8$ kJ.mol^{-1}) Although fluidized-bed reactors have been patented [10]. Fixed-bed, multitubular reactors (with tube sizes ranging from 1–400, i.e., 2.54–10.2 cm inside diameter, and tube lengths of 10–20 feet, i.e., 3.05–6.10 m) are almost exclusively used. In fixed-bed reactor systems, time-space yields of up to 300 kg.m^3/h are achievable. An average yield of 70–80 kg.m^3/h is maintained over the catalyst's lifetime. To prevent volatilization of the catalyst (tube side), temperature control and near-isothermal operation of the reactor are achieved using external cooling systems such as thermal oil or water [11].

The management of heat is a crucial aspect of reaction engineering design, aiming not only to enhance energy efficiency but also to prolong system lifespan and maintain operational stability [12]. Heat transfer processes are fundamental to achieving energy efficiency, making it essential to optimize heat transfer within the system for better performance [13]. In recent years, there has been a growing focus on reducing energy costs and improving overall operational efficiency. One effective approach to achieve these goals is efficient heat recovery, particularly in highly exothermic reactions. The heat of the reaction can be transferred and utilized in the reboilers of downstream purification equipment [14].

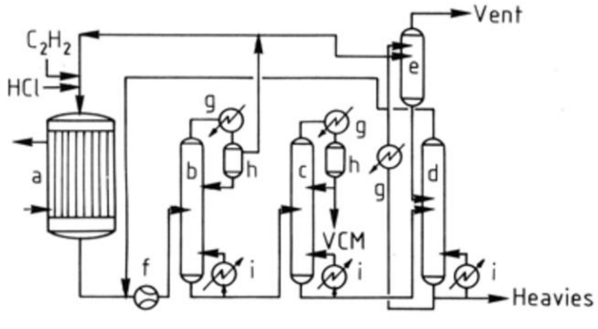

Figure 2. Production of vinyl chloride from acetylene and hydrogen chloride (schematic) [8]

Such reactions often produce substantial heat, part of which is typically lost or needs to be removed from the reactor to maintain the temperature within safe limits. This ensures product safety, quality, and system stability while preventing undesirable temperature increases [15]. In this study, the innovation involves utilizing the heat produced heat from the reactor's cooling process to improve overall energy utilization. Instead of discarding the heat, it is redirected to preheat other process streams, optimizing the thermal energy available in the system. By integrating heat recovery into the process, the modification ensures that energy is used more effectively, reducing the reliance on external heating sources. By comparing the heat efficiency of the modified process with the original design, the impact of the modification can be assessed. Calculating net energy provides a clear measure of the improvements made in energy recovery and utilization. This approach highlights the benefits of integrating heat recovery systems in industrial processes to achieve greater energy efficiency and cost-effectiveness.

As explained, VCM has a crucial role in the production of PVC in the industry. Development of VCM production still needs to be done in the future. A few researchers only focus on how to increase the yield of VCM production. This of course has been done a lot and many scientific researchers have been proven. However, there are no researchers who discuss the efficiency of energy use in the VCM industry. Therefore, this research is aimed to optimize heat efficiency in VCM production through acetylene hydrochlorination process by implementing heat transfer fluid looping system for heating and cooling, using Aspen HYSYS.

2. Methods

2.1 VCM Production

VCM production from acetylene hydrochlorination which is exothermic with high selectivity, and the optimum reaction temperature is 170–180 °C [16]. The reaction is represented as (Figure 1) [17]:

$$C_2H_2 + HCl \rightarrow CH_2{=}CHCl \quad \Delta H_{298} = -124.8 \text{ kJ/mol} \tag{1}$$

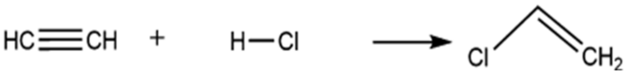

Figure 1. Hydrochlorination of acetylene [27].

This study discusses an industrial reactor used in the production of vinyl chloride monomer (VCM) through the acetylene hydrochlorination process. The catalyst commonly used for this process is 5–12 wt% $HgCl_2$ with high surface area carbon activated [18]. The reactor operates with a fixed-bed configuration featuring multiple parallel tubes. The small tube diameter (*dt*) and high gas velocity result in negligible axial dispersion within the tubes. The reactor operates under conditions of 0.1–0.5 MPa pressure and a temperature range of 120–200 °C, optimized to enhance the reaction and catalyst activity. These conditions ensure efficient VCM production while maintaining process stability and optimal catalyst performance [19].

2.2 Thermodynamic Review

A thermodynamic review is used to determine the characteristics of the reaction, described by the values of ΔH_r, ΔG_r, and K [20]. The hydrochlorination acetylene reaction will occur in a packed bed reactor. Data $\Delta H^0{}_{f\,298K}$ of each component to determine ΔH_r at 298 K can be seen in Table 1. The value of $\Delta H^0{}_{r\,298K}$ for the reaction of hydrochlorination acetylene is obtained by:

$$\Delta H^0{}_{r\,298K} = \sum \Delta H^0{}_{f\,298K\,product} - \sum \Delta H^0{}_{f\,298K\,reactant} \qquad (2)$$
$$\Delta H^0{}_{r\,298K} = \Delta H^0{}_{f\,298K\,C_2H_3Cl} - (\Delta H^0{}_{f\,298K\,C_2H_2} + \Delta H^0{}_{f\,298K\,HCl})$$
$$\Delta H^0{}_{r\,298K} = \left(28.5 - \left(228.2 + (-92.3)\right)\right)\,\mathrm{kJ/mol}$$
$$\Delta H^0{}_{r\,298K} = -107.4\ \mathrm{kJ/mol}$$

Based on the calculation, obtained $\Delta H^0{}_{r\,298K} = -107.4$ kJ/mol with negative value that indicates the reaction is exothermic. Data $\Delta G^0{}_{f\,298K}$ of each component to determine ΔG_r at 298 K can be seen in Table 2. The value of $\Delta G^0{}_{r\,298K}$ for the reaction of hydrochlorination acetylene is obtained by:

$$\Delta G^0{}_{r\,298K} = \sum \Delta G^0{}_{f\,298K\,product} - \sum \Delta G^0{}_{f\,298K\,reactant} \qquad (3)$$
$$\Delta G^0{}_{r\,298K} = \Delta G^0{}_{f\,298K\,C_2H_3Cl} - (\Delta G^0{}_{f\,298K\,C_2H_2} + \Delta G^0{}_{f\,298K\,HCl})$$
$$\Delta G^0{}_{r\,298K} = (41.4 - (210.7 + (-228.6)))\,\mathrm{kJ/mol}$$
$$\Delta G^0{}_{r\,298K} = 59.6\ \mathrm{kJ/mol}$$

Based on the calculation, obtained $\Delta G^0{}_{r\,298K} = 59.6$ kJ/mol with positive value that indicates the reaction is not spontaneous hence the need for a catalyst.

The value of equilibrium constant (*K*) at 298 K can be calculated by:

$$\ln K_{298} = \frac{-\Delta G^0{}_{r\,298K}}{RT} \qquad (4)$$
$$\ln K_{298} = \frac{-\left(59600\,\frac{\mathrm{J}}{\mathrm{mol}}\right)}{8.314\,\frac{\mathrm{J}}{\mathrm{mol.K}} \times 298\ \mathrm{K}}$$
$$\ln K_{298} = -24{,}056$$
$$K_{298} = 3.570 \times 10^{-11}$$

For the reaction temperature 180℃ or 453.15 K, the equilibrium constant (*K*) can be calculated by:

$$\ln \frac{K_{453.15}}{K_{298}} = \frac{\Delta H^0{}_{r\,298K}}{R} \times \left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \qquad (5)$$
$$\ln \frac{K_{453.15}}{3.570 \times 10^{-11}} = \frac{-107400\,\frac{\mathrm{J}}{\mathrm{mol}}}{8.314\,\frac{\mathrm{J}}{\mathrm{mol.K}}} \times \left(\frac{1}{453.15\ \mathrm{K}} - \frac{1}{298\ \mathrm{K}}\right)$$
$$\ln \frac{K_{453.15}}{3.570 \times 10^{-11}} = 14.842$$
$$K_{453.15} = 9.965 \times 10^{-5}$$

Based on the calculation, the equilibrium constant value of the reaction operates at 180 ℃ ($K_{453.15}$) = 9.965×10^{-5}, so the reaction is irreversible.

2.3 Energy Optimization Method

In order to enhance heat efficiency in the acetylene hydrochlorination process, simulations are conducted using Aspen HYSYS. The process employs a packed-bed reactor, where the reaction takes place under isothermal conditions. If this process remains isothermal but still generates heat that can be utilized, the process can still improve heat efficiency in a different way [21]. Although the reaction occurs at a constant temperature (isothermal), the heat generated can be redirected for use in other processes or to preheat the incoming reactor streams [22]. In this scenario, the generated heat not only maintains the reactor's temperature but can also be used to produce superheated steam for other reactions. This approach allows for more efficient energy use, even under isothermal conditions, by utilizing the heat produced to enhance the overall efficiency of the process.

In this modification, the heat received by the fluid from the reactor cooling process is used to heat the acetylene from 114.5 ℃ to 180 ℃. The fluid that comes out of the acetylene heating process still has a high temperature so that it can be reused to heat HCl from a temperature of 58.89 ℃ to 180 ℃ which the HCl then becomes feed to the reactor along with acetylene. The fluid that comes out of the HCl heating process is cooled using cooling water so that the fluid can be reused to cool the reactor as previously described. The heat efficiency of both basic and modified processes can be compared using net energy calculations as described by the formula:

$$NE = EP - EC \qquad (6)$$

Where *NE* represents the net-energy (in kJ/h), *EP* denotes the energy produced (in kJ/h), and *EC* refers to the energy consumed (in kJ/h) [23]. The impact of this modification process is analyzed.

3. Results and Discussion

3.1 Comparison Between Basic and Modified Processes

The simulation of VCM production through acetylene hydrochlorination process for the basic and modified processes using Aspen HYSYS is shown in Figures 3-6. The simulation of the basic process is shown in Figure 3 while the PFD of the basic process is shown in Figure 5. In the basic process, less equipment is used and there is no attempt to use the heat generated by the reactor (R-01) since the reaction is exothermic. On the other hand, the simulation of the modified process is shown in Figure 4 while its PFD is shown in Figure 6. In the modified process, more equipment is used because it aims to utilize the heat generated by the reactor (R-01). The difference between the two processes is the addition of a heat transfer process fluid looping system to heating the reactor feed and cooling the reactor as can be seen in the modified process. In the basic process, there is no use of heat transfer with a fluid looping system so that the energy produced by the reactor (R-01) is wasted and does not run efficiently. But in the modified process, there is the addition of a heater (E-101) which has the same heat value as the reactor so that it is a parable that the fluid is flowed to cool the reactor. Then there are also additional heat exchangers (HE-01 and HE-02) to heat the reactor feed. Heat exchanger (RE-01) with cooling water as a cold fluid is used to cool the heated fluid in HE-02 so that the fluid can be used to cooling the reactor again and a fluid looping system is formed.

3.2 Mass Balance and Energy Balance Results

Based on Table S1 (Supporting Information), the mass balance and heat balance for the modified process have been reported. In Figure 4, it is shown that the heater (E-101) is used to cool the reactor (R-01) with a mass flow rate of Dowtherm A fluid of 174,351.4 kg/h from a temperature of 60.03 ℃ to 210 ℃. The heat generated from the reactor (R-01) is received by the fluid of 38,923,405.438 kJ/h. The hot fluid generated from the process is flowed to the heat exchanger (HE-01) to increase the temperature of acetylene from 114.5 ℃ to 180 ℃ with a mass flow rate of acetylene of 9,962 kg/h and a total duty of 1,285,718.762 kJ/h. The hot fluid leaving the heat exchanger (HE-01) is reused in the heat exchanger (HE-02) to heat HCl from 58.89 ℃ to 180 ℃ with a mass flow rate of HCl of 70,512.434 kg/h and a total duty of 7,146,045.979 kJ/h. Meanwhile, the heat exchanger (RE-01) is used to

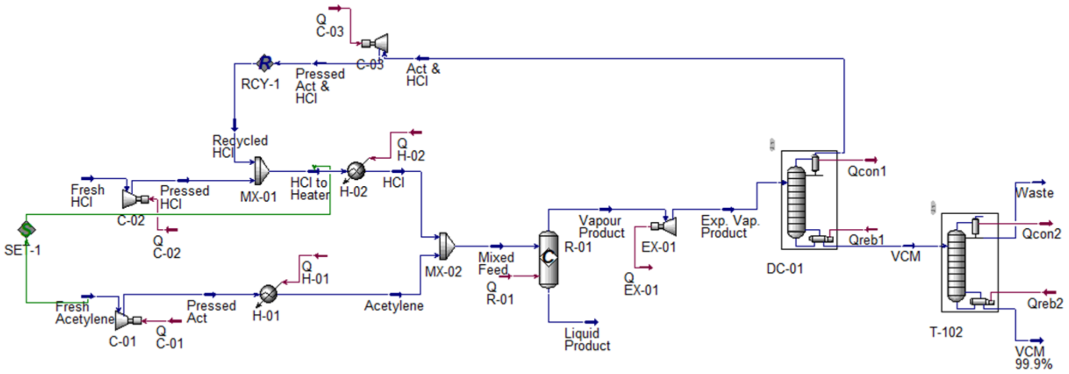

Figure 3. Simulation using Aspen HYSYS of basic (unmodified) process

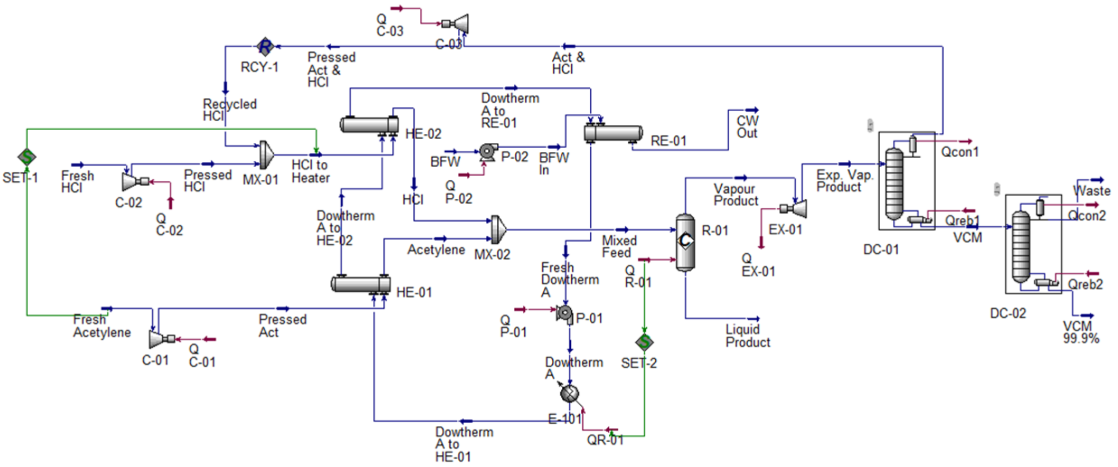

Figure 4. Simulation using Aspen HYSYS of modified process

re-cool the Dowtherm A fluid that has been used in HE-01 & HE-02 to heat the reactor feed. The re-cooling process changes the temperature of Dowtherm A fluid from 182.1 ℃ to 60 ℃ using water with a mass flow rate of 11,391.805 kg/h at 30.05 ℃ as a coolant and obtaining heat of 30,510,343.648 kJ/h from Dowtherm A. Then, the heat exchanger fluid recycle process continues.

3.3 Choosing Heat Transfer Fluid

Heat transfer circulation that occurs in the VCM manufacturing process is to heat or cool the compounds. In the unmodified process, the heat transfer that occurs is in the operating unit in the form of a heater and cooler with external energy as a heat source. Whereas in the modified process, heat transfer occurs more often due to the replacement of cooler and heater operating units that utilize heat energy from outside replaced with heat exchanger units as heat transfer media. In this scenario, the heating fluid used in the heat exchanger circuit is Dowtherm A. In the simulation of Figure 6, Dowtherm A will be circulated in a loop to heat the compound and make steam in the reboiler for other utility purposes. When steam is heated above its boiling point for a given pressure, hot dry steam often referred to as superheated steam is formed [24]. In addition, Dowtherm A with a lower temperature due to steam generation, is used as a reactor coolant. The VCM formation reaction is an exothermic and highly selective with an optimum reaction temperature of 170-180 °C, with a negative delta H value that can generate heat [25]. The heat generated by the reactor is utilized to recover heat loss in Dowtherm A which is decreasing in temperature as a heating fluid so that Dowtherm A temperature rises again.

3.4 Utilizing Heat Exchange between Process Stream

In the first stage of distillation, the top product in the form of HCl is fed back to be mixed with fresh feed that goes to the reactor through the recycle process. HCl in the distillation top product has an output temperature of 26.33 °C, this temperature needs to be increased before entering the reactor. In Figure 5, the unmodified

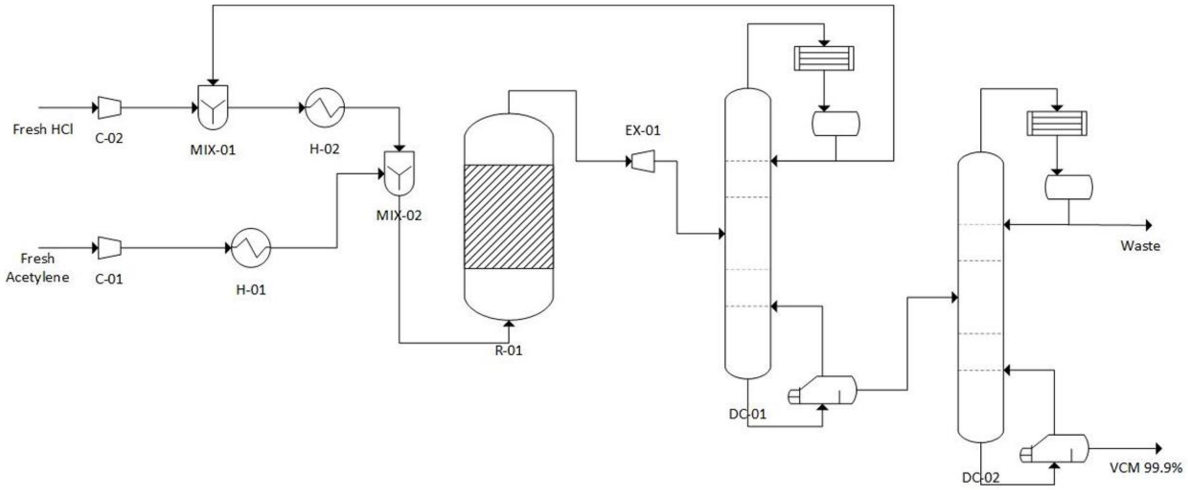

Figure 5. Process flow diagram of basic (unmodified) process

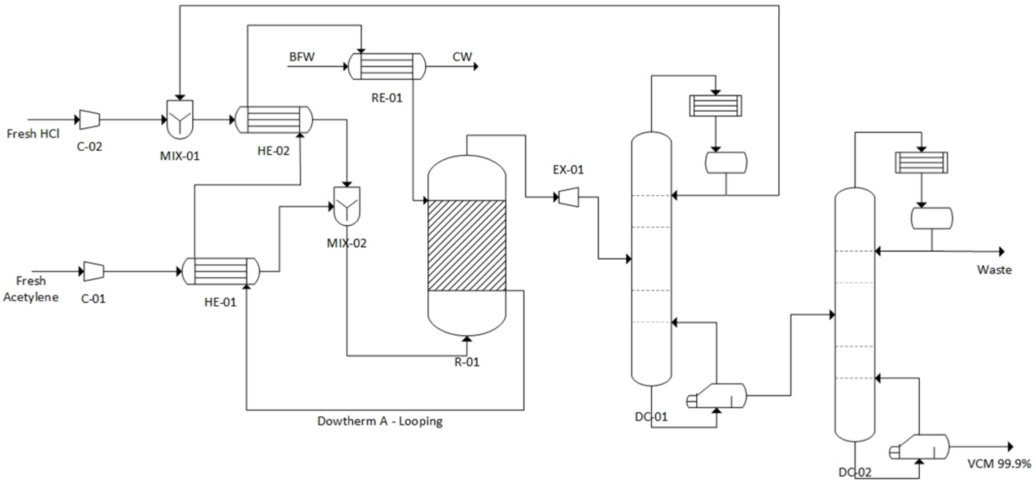

Figure 6. Process flow diagram of modified process

process uses a heater unit (H-02) to increase the temperature of the HCl stream with an external heat source. Likewise, the acetylene feed, a heater (H-01) is used to directly increase the feed temperature before entering the reactor. Whereas in Figure 6, the process that has been modified the heater operating units (H-01 and H-02) are converted into shell and tube heat exchangers (HE-01 and HE-02). The heat energy used to increase the temperature of the HCl and acetylene feeds comes from the dowtherm A heating fluid which is circulated in a loop. The energy usage of heat exchangers is more efficient than using heaters, because the heat energy comes from a continuously circulated heating fluid with heat regeneration coming from exothermic reactions in the reactor.

3.5 Net-Energy Efficiency Improvement Due to Process Modification

The total Net-Energy for both the basic and modified processes is shown in Table 1. In the basic process, the value of *EP* is 38,811,930.515 kJ/h which is obtained from the heat generated by the reactor because the reaction is exothermic. However, the value of *EC* is equal to zero because there is no reuse of the heat generated. On the other hand, the modified process has an *EP* value of 38,923,405.438 kJ/h which is obtained from the heat generated by the reactor and Dowtherm A is used to cool the reactor. The *EC* value is 38,942,108.389 kJ/h because it is used for reactor feed heating of 8,431,764.741 kJ/h and Dowtherm A re-cooling of 30,510,343.648 kJ/h. It can be concluded that the net-energy (*NE*) in the basic process is 38,811,930.515 kJ/h and in the modified process is 18,702.951 kJ/h.

In the discussion of energy efficiency, net-energy that is closer to zero will be better in terms of energy produced or used [26]. In this study, it can also be seen that the net-energy in the modified process has a smaller value. It can be concluded that the modified process has better energy efficiency than the basic process.

4. Conclusion

The heat transfer fluid circulation system for the heating and cooling process enhances the thermal efficiency of vinyl chloride monomer (VCM) production via the acetylene hydrochlorination method. This improvement is evidenced by the net-energy value of the modified system, which is 18,702.951 kJ/h, compared to 38,811,930.515 kJ/h in the conventional process. The significant reduction in the net-energy value of the modified process, bringing it closer to zero, indicates far better energy performance. The circulation mechanism in the heat exchange fluid facilitates improved energy utilization by enabling energy release and reception within the system, which can be efficiently shared across different stages of the process.

CRediT Author Statement

Author Contributions: R. Apriyani: Conceptualization, Methodology, Investigation, Software, Visualization, Writing, Review & Editing, Project Administration, Supervision; R. P. N. Alim: Conceptualization, Methodology, Visualization, Software, Writing, Review & Editing, Validation; R. Mustaqim: Conceptualization, Methodology, Formal Analysis, Software, Resources, Validation, Writing, Revieww & Editing; F. S. Prasetya: Conceptualization, Methodology, Software, Investigation, Resources, Data Curation, Writing, Review & Editing. All authors have read and agreed to the published version of the manuscript.

Table 1. $\Delta H°_{f\,298K}$ data for each component [28]

Component	$\Delta H^0_{f\,298K}$
C_2H_3Cl	28.5
C_2H_2	228.2
HCl	-92.3

Table 2. $\Delta G°_{f\,298K}$ data for each component [28]

Component	$\Delta G^0_{f\,298K}$
C_2H_3Cl	41.1
C_2H_2	210.7
HCl	-228.6

Table 3. Calculation result of net-energy of basic and modified process

Type of Process	*EP* (kJ/h)	*EC* (kJ/h)	*NE* (kJ/h)
Basic	38,811,930.515	0	38,811,930.515
Modified	38,923,405.438	38,942,108.389	18,702.951

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