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Research Article

Minimizing Process Water and Energy Consumption in Styrene Production by Ethylbenzene Dehydrogenation

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Abstract

Styrene is a crucial unsaturated aromatic monomer with a wide range of industrial applications. Styrene production faces several problems where the water supply and energy usage are keep increasing. Process modifications were implemented to minimize process water and to optimize the energy consumption. The modification uses Aspen HYSYS simulation by replacing coolers and heaters with heat exchanger and implementing water recycling system. Aspen HYSYS simulations show these changes reduce water usage by 89.8% and significantly decrease energy consumption up to 54.69%. This modification shows the water and energy usage have been significantly reduced than the basic process.

Keywords: Styrene; Process water minimization; Net energy; Process modification; Ethylbenzene Dehydrogenation

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1. Introduction

Styrene, $C_6H_5–CH=CH_2$, also known as phenylethylene, vinylbenzene, styrol, or cinnamene, is a crucial unsaturated aromatic monomer with a wide range of industrial applications. Originally distilled from natural balsam storax in the 19th century, styrene is now primarily derived from coal tar and can also be found in everyday items like peanuts, coffee beans, and cinnamon [1]. The production of styrene is divided into four consists, ethylbenzene dehydrogenation [2], from propylene oxide [3], from butadiene [4], and the reaction of toluene and methanol [5].

In the world of manufacturing, styrene plays a key role in the production of polystyrene (PS), a versatile polymer widely used in packaging materials. Molded polystyrene finds its way into various products, including furniture, automobile interiors, and household appliances. Beyond this, styrene is essential for the synthesis of copolymers such as Acrylonitrile Butadiene Styrene (ABS), which is used in vehicle construction. Additionally, styrene contributes to the production of latex, rubber, and carpet backing, making it indispensable in a variety of industries [6].

Since the 1930s, commercial methods based on the dehydrogenation of ethylbenzene were developed to produce styrene. Currently, the catalytic dehydrogenation of ethylbenzene accounts for approximately 90% of global styrene production, making it a cornerstone of the industry. Various methods exist for producing styrene monomer from ethylbenzene, including adiabatic dehydrogenation, isothermal dehydrogenation, simultaneous styrene production with propylene oxidation, membranous dehydrogenation, and the use of carbon dioxide for dehydrogenation and oxidation. Among these,

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adiabatic dehydrogenation remains the most widely adopted approach [7].

However, this method faces several significant challenges such as the high steam-to-ethylbenzene ratio, limited conversion efficiency due to thermodynamic equilibrium constraints, complex product separation, and substantial energy demands. These issues highlight the urgent need for innovative solutions to enhance styrene production efficiency and overcome the inherent limitations of the current catalytic dehydrogenation processes [8].

In an effort to enhance styrene production from both an economic and operational standpoint, this research will explore the design of a styrene plant through simulations that prioritize energy efficiency. Studies suggest that addressing energy challenges in this field can be achieved by integrating sustainable design practices at various stages of the production process. Optimizing energy use is not only vital for improving industry performance but also aligns with broader sustainability goals within the industrial sector.

Based on previous research on energy efficiency of styrene production, this research focused on energy efficient ethylbenzene to styrene processes combined with water recycling. The primary objective of this research is to minimize the process water and enhance net energy efficiency in the production of styrene, offering a more sustainable approach to this vital industrial process.

2. Methods

2.1 Process Simulators used for Evaluation

Process simulation plays a crucial role in process engineering, helping to improve system control and maintenance amid operational challenges, regulations, and market competition. Simulators like Aspen Plus, Aspen HYSYS, and others are essential tools for developing accurate models to understand plant behavior during operations [9]. These tools allow engineers to perform complex calculations efficiently [10].

Aspen HYSYS, widely used in the oil, gas, and refining industries, provides a strong thermodynamic foundation for accurate property and phase behavior calculations [11]. It offers various thermodynamic models, enabling engineers to select the most appropriate for analyzing phase equilibrium and compound enthalpy. In the simulation process for dehydrogenation Ethylbenzene in styrene production, the Peng-Robinson (PR) property package was used for optimization.

2.2. Description of Process

Styrene (ST) is the second principal monomers in the chemical industries because it is a key raw material of polymers. The major commercial process to produce styrene is the dehydrogenation of ethylbenzene (EB), in which adiabatic dehydrogenation accounts to 90% of the commercial production [12]. The ethylbenzene dehydrogenation process can be accomplished either adiabatically or isothermally. Over 75% of all operating styrene plants carry out the dehydrogenation reaction adiabatically [13]. The EB dehydrogenation is carried out in three adiabatic reactors put in series. There are significant parameters to take into account in the case of this reaction. Firstly, the EB dehydrogenation is endothermic and reversible.

The reaction is the following:

$C_6H_5CH_2CH_3$ (ethyl benzene) ⇌ $C_6H_5CHCH_2$ (styrene) + H_2 (hydrogen) (1)

In addition, several side reactions can occur, such as [9]:

$C_6H_5CH_2CH_3 \rightarrow C_6H_6$ (Benzene) + C_2H_4 (Ethylene) (2)

$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3$ (Toluene) + CH_4 (Methane) (3)

The dehydrogenation ethylbenzene reaction to styrene is carried out catalytically. The primary reaction that takes place in the vapor phase is assisted by steam and a solid catalyst of iron oxide [14]. Several catalyst properties information used in the simulation includes the bulk density of the catalyst and the fixed-bed void fraction, which are 2146 kg/m^3 and 0.445, respectively [13]. The reaction is over a temperature range of 540-650 °C [14]. In this simulation, the adiabatic reactor input stream temperature is set at 650 °C. The operating pressure for reactors should be from 1.2 to 3 bar [13]. The function of steam is to provide heat for reaction, to shift the reaction equilibrium towards the product, and restrain formation carbon on the catalyst [14]. The ratio between steam and ethylbenzene before proceeding to reactors is 13 [13].

2.3. Method to Improve Net Energy Efficiency of Styrene Production

In an industrial setting, energy plays a crucial role as one of its most essential components. This is because nearly every operation relies on some form of energy. It is vital for industrial activities to have access to an energy source, which could include electricity or other forms of energy such as fuel, coal, charcoal, firewood, and similar resources [15]. As the global industrial sector expands, the demand for energy increases in parallel, posing significant challenges both economically and environmentally [16]. One way energy can be conserved is through optimization of the production process itself [17]. Optimization can be achieved in several ways, one of them is to increase the efficiency of the equipment used in the process itself [18].

Modifications are made to optimize the net energy and minimize process water of styrene production. The modification uses heat exchanger to substitute the heater and cooler in order to optimize the energy consumption. Afterwards, in minimizing the process water supply, water result from triple separator is being used for heat exchanger to be a cooler and its steam will be being recycled to support the steam making in first mixer.

3. Results and Discussion

3.1. Comparison Between Basic and Modified Process

The simulation of styrene production through the ethylbenzene dehydrogenation process, for both the basic and modified processes, using Aspen HYSYS is shown in Figures 1-4. The

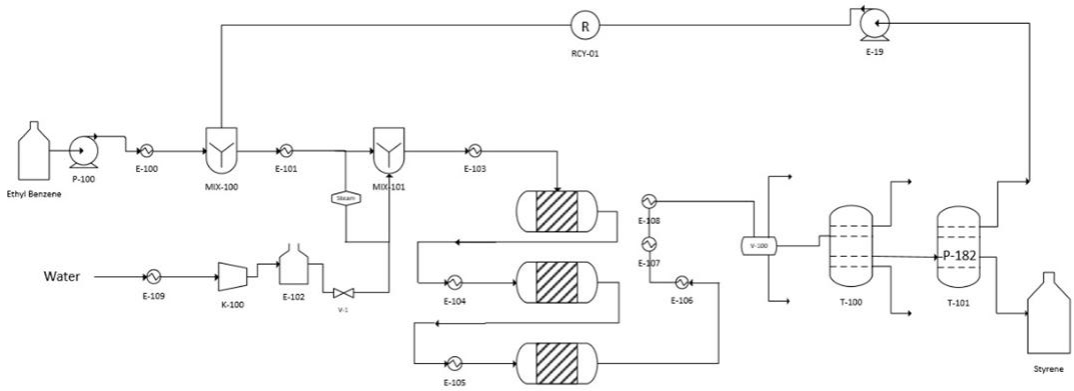

Figure 1. Process Flow Diagram (PFD) of basic (unmodified) process [13]

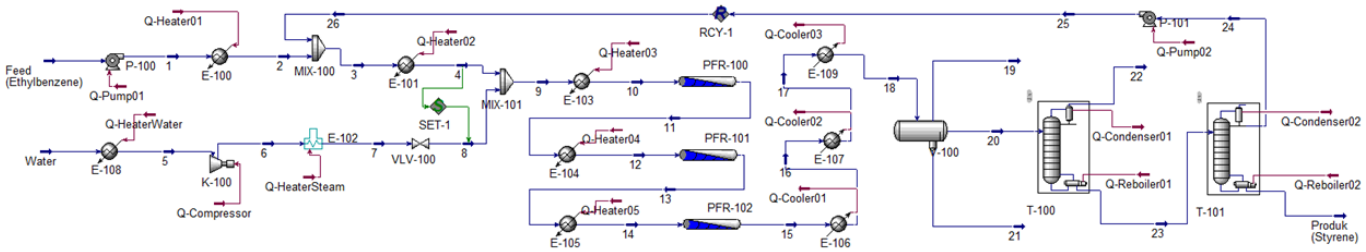

Figure 2. Aspen HYSYS simulation of basic (unmodified) process

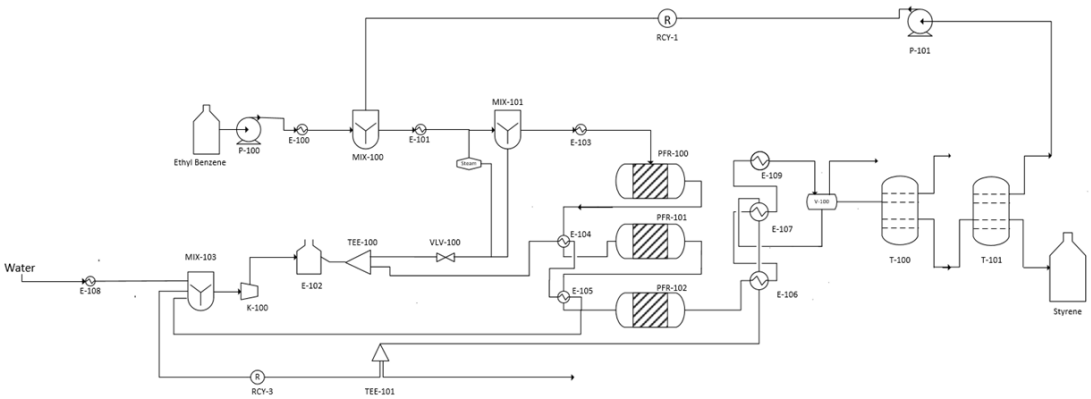

Figure 3. Process Flow Diagram (PFD) of modified process

basic process flow diagram (PFD) is presented in Figure 1, while the process simulation is shown in Figure 2. In the basic process, there is only one recycle stream from the top of the second distillation column (T-101), which is recycled and re-mixed with pure ethylbenzene feed in the mixer (MIX-100). In contrast, the modified PFD is shown in Figure 3, and the process simulation for the modified system is shown in Figure 4. In the modified process, there are two recycle streams. The first recycle stream is identical to the one in the basic process. The second recycle stream involves steam used for the reaction. After being cooled and split by the conditional fraction (TEE-101), this stream is recycled and re-mixed with pure water in the mixer (MIX-103). Additionally, in the modified process, the heaters and coolers used in the basic process are replaced with heat exchangers for more efficient thermal management.

3.2. Thermodynamics Review

For the determination of the nature of the reaction (exothermic/endothermic) and the direction of the reaction (reversible/irreversible), it is necessary to calculate the standard heat of reaction ($\Delta H°_{298K}$) at 1 bar and 298 K based on standard heat of formation of the reactants and products. The value of $\Delta H_f°$ and $\Delta G_f°$ of compounds can be seen in Table 1.

Standard heat calculation for each reaction:

Based on the Table 1 :

$$\Delta H^{\circ}_{298K} = \left(\Delta H^{\circ}_f\ C_6H_5CHCH_2 + \Delta H^{\circ}_f\ H_2\right) - \left(\Delta H^{\circ}_f\ C_6H_5CH_2CH_3\right)$$

$$= \sum \Delta H^{\circ}_f\ product - \sum \Delta H^{\circ}_f\ reactan$$

(1) $C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2$

$\Delta H^{\circ}_{298K} = 118.4$ kJ/mol

(2) $C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$

$\Delta H^{\circ}_{298K} = 105.5$ kJ/mol

(3) $C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$

$\Delta H^{\circ}_{298K} = -54.2$ kJ/mol

$$\Delta H_{total\ reaction} = \Delta H_{f\ reaction\ 1} + \Delta H_{f\ reaction\ 2} + \Delta H_{f\ reaction\ 3}$$

$$\Delta H_{total\ reaction} = 169.7\ kJ/mol$$

Based on the calculations, we get the value $\Delta H_{total\ reaction}$=169.7 kJ/mol, which is a positive value so that the reaction is endothermic.

Calculation of ΔG_f reaction (1) as a main reaction:

$$\Delta G_{f\ reaction} = \Delta G_{f\ product} - \Delta G_{f\ reactant}$$

$$\Delta G_{f\ reaction} = (G_f\ C_6H_5CHCH_2 + G_f\ H_2) - (G_f\ C_6H_5CH_2CH_3)$$

$$\Delta G_{f\ reaction} = 84.3\ kJ/mol\ = 84{,}300\ J/mol$$

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

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

$$ln\ K_{298} = \frac{84{,}300\ J/mol}{-\left(8.314 \frac{J}{mol.K}\right)(298\ K)}$$

$$ln\ K_{298} = -34.023$$

$$K_{298} = 1.675 \times 10^{-15}$$

At operating temperature of 650 °C (923.15 K):

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

Table 1. The value of ΔHf° and ΔGf° of compounds

Components	Molecular Formula	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)
EthylBenzene	$C_6H_5CH_2CH_3$	29.9	130.7
Styrene	$C_6H_5CH{=}CH_2$	148.3	215
Hydrogen	H_2	0	0
Toluene	$C_6H_5CH_3$	50.2	122.3
Methane	CH_4	-74,5	-50.5
Benzene	C_6H_6	82.9	129.8
Ethylene	C_2H_4	52.5	68.5

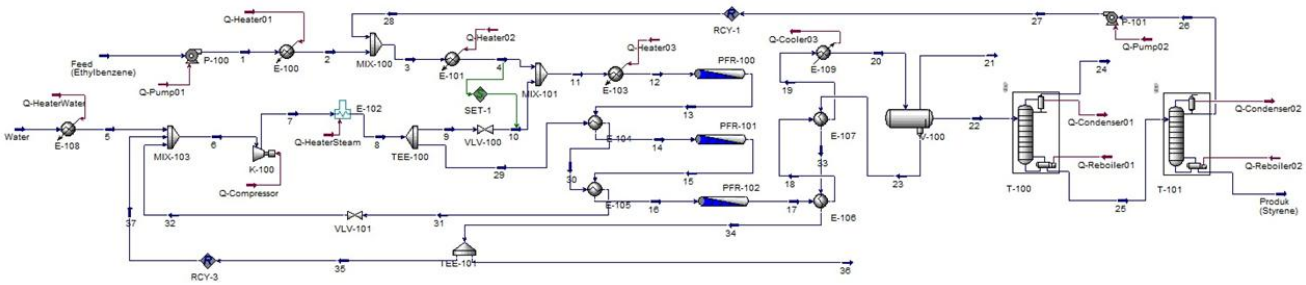

Figure 4. Aspen HYSYS simulation of modified process.

$$ln\left(\frac{K_{923.15}}{1.675 \times 10^{-15}}\right) = -\frac{118{,}400\ J/mol}{8.314\frac{J}{mol.K}}\left(\frac{1}{923.15\ K} - \frac{1}{298\ K}\right)$$

$$ln\left(\frac{K_{923.15}}{1.675 \times 10^{-15}}\right) = 32.360$$

$$K_{923.15} = 0.190$$

Because the value of $K_{923.15}$ < 1, thus, the first reaction (main reaction) is reversible. A small value of equilibrium constant indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Calculation of ΔG_f reaction (2) as a side reaction:

$$\Delta G_{f\ reaction} = \Delta G_{f\ product} - \Delta G_{f\ reactant}$$

$\Delta G_{f\ reaction}$ = (G_f C_6H_6 + G_f C_2H_4) – (G_f $C_6H_5CH_2CH_3$)

$$\Delta G_{f\ reaction} = -31.9\ kJ/mol = -31{,}900\ J/mol$$

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

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

$$ln\ K_{298} = \frac{-31{,}900\ kJ/mol}{-\left(8.314\frac{J}{mol.K}\right)(298\ K)}$$

$$ln\ K_{298} = -27.283$$

$$K_{298} = 1.416 \times 10^{-12}$$

At operating temperature of 650 ℃ (923.15 K):

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

$$ln\left(\frac{K_{923.15}}{1.416 \times 10^{-12}}\right) = -\frac{105{,}500\ \text{J/mol}}{8.314\frac{J}{mol.K}}\left(\frac{1}{923.15\ K} - \frac{1}{298\ K}\right)$$

$$ln\left(\frac{K_{923.15}}{1.416 \times 10^{-12}}\right) = 28.834$$

$$K_{923.15} = 4.718$$

Because the value of $K_{923.15}$ > 1, thus, the second reaction (side reaction) is irreversible.

Calculation of ΔG_f reaction (3) as a side reaction:

$$\Delta G_{f\ reaction} = \Delta G_{f\ product} - \Delta G_{f\ reactant}$$

$\Delta G_{f\ reaction}$ = (G_f $C_6H_5CH_3$ + G_f CH_4) – (G_f $C_6H_5CH_2CH_3$ + G_f H_2)

$$\Delta G_{f\ reaction} = -58.9\ kJ/mol = -58{,}900\ J/mol$$

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

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

$$ln\ K_{298} = \frac{-58{,}900\ J/mol}{-\left(8.314\frac{J}{mol.K}\right)(298\ K)}$$

$$ln\ K_{298} = 23.772$$

$$K_{298} = 2.109 \times 10^{-10}$$

At operating temperature of 650℃ (923.15 K):

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

$$ln\left(\frac{K_{923.15}}{2.109 \times 10^{-10}}\right) = -\frac{-54{,}200\ \text{J/mol}}{8.314\frac{J}{mol.K}}\left(\frac{1}{923.15\ K} - \frac{1}{298\ K}\right)$$

$$ln\left(\frac{K_{923.15}}{2.109 \times 10^{-10}}\right) = -14.814$$

$$K_{923.15} = 7772.176$$

Because the value of $K_{923.15}$ > 1, thus, the third reaction (side reaction) is irreversible.

3.3 Process Modification: Improving Net Energy of Styrene

The modification process to improving net energy of production styrene can be modified in a various way. In this study, heat exchanger is used to substitute the cooler and heater to improve the net energy. The selection for the use of a heater-cooler or heat exchanger is based on the presence or absence of a heat transfer fluid that can be utilized to heat the feed. If there is a heat transfer fluid, then the use of a heat exchanger is preferred over a heater. But, if there is no heat transfer fluid, then the use of a heater is selected by using additional energy. The use of heat exchangers will be more efficient in terms of energy used because it does not require additional energy during the process. In addition, the heat exchanger also has two functions because it can be used to heating and cooling the fluid that enters the heat exchanger by transferring heat between two fluids that have a difference in temperature where the two fluids are arranged separately and given a barrier in the form of a wall with the aim of preventing mixing between those two [19,20]. While the heater and cooler only has one function to increase the temperature of the fluid that enters the heater so that it requires additional energy during the process [21]. This strategic integration not only maximizes the utilization of thermal energy but also contributes to the overall sustainability and efficiency of the process [22].

In the modification process, only two heaters (E-104 and E-105) and two coolers (E-106 and E-107) that are being replaced. The reason of this placement is to ensure the inlet temperature to the reactor (PFR-100) and decreasing the vapor fraction amount as an inlet for the triple separator (V-100). The cooler and heater is also still used as a controller to give addition energy.

3.4 Process Modification: Minimizing Process Water by Water Recycle

Water plays an important role in industry and needs to being used as efficient as it can. The implementation of water minimization techniques can significantly lower the overall demand for fresh water in various processed and in turn, decrease the volume of wastewater produced [23]. In this modification (Table 2), water remaining (Stream 23) from triple separator (V-100) has a huge potential for being recycled. The water from Stream 23 is used for Heat Exchanger to cool down the output of reactor (Stream 17). After the steam (Stream 34) temperature has decreased, steam can also be recycled by using splitter (TEE-101) in supporting the steam production in the first mixer (MIX-103).

The efficiency of minimizing process water has a satisfy result which is 89.8% more efficient and the output of water also decreased to 90%. This efficiency of using water has shown that the modified process also gives an environment impact in reducing water supply.

3.5 Energy Analysis between Unmodified and Modified Processes

After the simulation, data on the total energy required by the system can be obtained. This energy is measured through the heat flow (kJ/h) of the system itself. This method serves as an analogy for how much energy can be conserved compared to the unmodified system. From there, we can mathematically measure the energy saved by the modified process and assess its efficiency. The heat stream data obtained from the simulation is presented in Table 3. It is known that the amount of heat flow in the simulation before and after modification has decreased, which shows considerable energy efficiency 54.69%. In addition to less energy used, this also indirectly reduces the number of tools used such as cooler and heaters.

Table 2. The input and output of water in unmodified and modified process

Unmodified Process		Modified Process	
Stream	Mass Flow (kg/h)	Stream	Mass Flow (kg/h)
Water (Input)	12470	Water (Input)	1268
21 (Output)	12450	36 (Output)	1245

Table 3. Energy analysis of the unmodified and modified processes

Unmodified Process		Modified Process	
Heat stream items	Heat flow (kJ/h)	Heat stream items	Heat flow (kJ/h)
Q-Pump01	3.540E+02	Q-Pump01	3.540E+02
Q-Pump02	2.449E+02	Q-Pump02	2.449E+02
Q-Compressor	3.520E+06	Q-Compressor	1.620E+07
Q-Heater01	9.453E+05	Q-Heater01	9.454E+05
Q-Heater02	3.107E+06	Q-Heater02	3.107E+06
Q-Heater03	1.958E+06	Q-Heater03	1.958E+06
Q-Heater04	3.924E+06	Q-Heater04	-
Q-Heater05	4.142E+05	Q-Heater05	-
Q-HeaterWater	3.234E+07	Q-HeaterWater	3.289E+06
Q-HeaterSteam	1.426E+07	Q-HeaterSteam	5.891E+05
Q-Cooler01	1.239E+07	Q-Cooler01	-
Q-Cooler02	2.566E+07	Q-Cooler02	-
Q-Cooler03	1.803E+07	Q-Cooler03	1.803E+07
Q-Condenser01	5.739E+05	Q-Condenser01	5.739E+05
Q-Condenser02	6.867E+06	Q-Condenser02	6.869E+06
Q-Reboiler01	2.046E+06	Q-Reboiler01	2.046E+06
Q-Reboiler02	6.379E+06	Q-Reboiler02	6.381E+06
Total	1.324E+08	Total	5.999E+07

4. Conclusion

Process modification in styrene production shows change in energy efficiency and process water feeds. Through the modifications, plant can optimize raw material and energy usage, reduce environmental impact, enhance product yield, and improve operational efficiency. According to the implemented modified process, there has been an improvement to the energy efficiency up to 54.69% and minimizing process water up to 89.8%. Further studies regarding the styrene dehydrogenation process are still needed, especially the environment impact. Analyzing the impact on the environment is also very important, considering that in this decade, the world is starting to take environmental problems seriously.

CRediT Author Statement

M.I. Najib: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing, Review and Editing, Supervision; F. Hestiawan: Conceptualization, Methodology, Formal Analysis, Data Curation, Writting Draft Preparation, Visualization, Software, Project Administration; A. Pratiwi: Validation, Writing, Review and Editing, Data Curation; L.B. Pangayom: Investigation, Resources, Writing, Review and Editing, Validation. All authors have read and agreed to the published version of the manuscript.

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