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Research Article

Energy Optimization of Dimethyl Ether (DME) Production Process from Methanol Dehydration

Al Fath Ghoffaru[1]*, Jovian Luxioctafiano Grasia[1], Athallah Akmal Wijaya[1], Narendra Dzaki Ramadhan[1], Andre Nur Saputro[1], Anggistia Maharani[2]

[1]*Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang, Indonesia*
[2]*Department of Chemical Engineering, Sebelas Maret University, Surakarta, Indonesia.*

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Abstract

The increasing demand for sustainable and clean alternative fuels has driven the focus on dimethyl ether (DME), an environmentally friendly and non-toxic chemical with high potential as a fuel and industrial solvent. DME can be produced from various raw materials such as natural gas, methanol, biomass, and coal. This study investigates the optimization of DME production from methanol dehydration using a fixed-bed plug flow reactor and γ-Al_2O_3 catalyst, emphasizing energy efficiency improvements. Modifications were implemented in the Aspen HYSYS simulation by replacing the conventional heater with heat exchanger and utilizing heat generated during cooling process for another heating process. The results demonstrated a significant reduction 65.8 % in net energy consumption from 8.54×10^6 kJ/h to 2.92×10^6 kJ/h, validating the effectiveness of these modifications by leveraging Aspen HYSYS simulations, the proposed design achieved high process efficiency while maintaining the target DME purity of 99.95 % produced. This research highlights the potential of heat integration strategies to enhance the economic and environmental performance of DME production processes.

Keywords: Optimization; dimethyl ether; methanol dehydration; simulation; DME

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1. Introduction

The increasing demand of alternative and clean fuels has led to the production of dimethyl ether (DME). DME as alternative fuels are very friendly to the environment, since the ether will not form explosive peroxide, allowing it to have safe storage. Furthermore, it has the advantage of decreasing emissions of NO_x, SO_x, and particulates over conventional diesel [1]. DME is the simplest ether, with the formula CH_3OCH_3 having a high cetane number and properties close to that of LPG, such as viscosity, boiling point, and pressure [2]. DME is produced from various raw materials such as natural gas, methanol, biomass, and coal. The low boiling point and zero sulphur content are the main properties of DME, which results in its continuous interest as a solvent in the chemical and petrochemical industries [3], thus the importance of DME has motivated numerous research to focus on investigation of various catalysts for methanol dehydration reaction [4].

At this moment, DME has been used as aerosol propellant to replace chlorofluorocarbon which can destroy the ozone layer [5]. DME can be produced by direct and indirect processes. In the indirect process, methanol is converted to DME over a solid-acid catalyst by the following reaction [6]:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad \Delta H^\circ_r = -23.54 \text{ kJ/mol} \quad (1)$$

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* Corresponding Author.
Email: alfathghoffaru@students.undip.ac.id (A. F. Ghoffaru)

This reaction occurs under certain conditions without producing a reaction side [7]. The acid catalyst belongs to the solid-acid catalyst class including γ-Al_2O_3 and its variously modified forms, zeolites, and ion exchange resins [8]. The Al_2O_3-based catalysts showed better DME selectivity because of the absence of stronger Bronsted acid sites compared to zeolite-based solid acid catalysts [9]. However, lower hydrothermal stability in the presence of water leads to deactivation of Al_2O_3 [10]. Alternatively, DME can be synthesized directly from coal, natural gas, and biomass via synthesis gas, i.e. a mixture of H_2, CO, and usually CO_2 gas [11]. In this process, the synthesis gas is mostly converted to methanol, followed by methanol dehydration to DME. The DME synthesis from dehydration of methanol with solid-acid catalyst process was chosen for this study due to its high conversion and low investment costs, as well as its growing significance on a global scale in terms of energy and environmental benefits [12].

In previous research, modifications have been performed in the simulation process for DME production such as changing reactor model and utilizing recycled products to increase the DME production [13]. Utilizing self-heat recuperation to increase the energy efficiency of the methanol to dimethyl ether process has also been simulated [14], but only the energy required for heat exchangers has been calculated. The aim of this study is to enhance heat energy efficiency in DME production by utilizing the heat generated from a cooler to reheat another heater and changing heater to heat exchanger using Aspen HYSYS.

2. Methods

2.1 Dimethyl Ether (DME) Production

Dimethyl ether (DME) is a versatile chemical compound also known as methoxy methane or methyl ether, exhibits properties similar to diesel gasoline and Liquefied Petroleum Gas (LPG) which is primarily a mixture of propane and butane [15], making it an appropriate alternative for fossil fuel. DME is conventionally produced in two steps, (indirect process) from syngas constituting CO, H_2, and CO_2 and (direct process) from methanol dehydration [16].

DME production from methanol dehydration involves the removal of water molecules from methanol through a catalytic dehydration reaction, which is exothermic (generates heat) and reversible [17]. The reaction is represented as [18]:

$$2\ CH_3OH_{(g)} \rightarrow CH_3OCH_{3\ (g)} + H_2O_{\ (g)} \quad (2)$$
$$CO_2 + 3H_2O \leftrightarrow CH_3OH_{(g)} + H_2O_{(g)} \quad (3)$$
$$CO + 2H_2 \leftrightarrow CH_3OH(g) \quad (4)$$
$$CO + H_2O_{(g)} \leftrightarrow CO_2 + H_2 \quad (5)$$

In this study, the process utilized in a fixed-bed plug flow reactor and γ-Al_2O_3 catalyst is loaded due to its high selectivity and stability under reaction conditions [19]. Fresh methanol is fed continuously then mixed with recycled streams in the vessel. The mixture is then pumped and preheated before entering the reactor. The reactor operates a methanol dehydration reaction at a temperature of 250 °C and a pressure of 10.75 bar.

The reactor, consisting of DME, water, and unreacted methanol, is sent to a condenser where it is partially liquefied. The pressure of the resulting mixture is adjusted with a control valve and routed to a secondary cooler, then subsequently to the first distillation column. Here, DME is separated as the overhead product, while the bottom product containing methanol and water is fed into a second distillation column for further separation. In T-101, unreacted methanol is recovered and recycled back to the process to maximize resource efficiency, while water is removed as wastewater. Therefore, the final DME product is obtained. A simple block diagram of the overall process of DME synthesis from methanol dehydration is shown in Figure 1.

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 [21]. The methanol dehydration reaction will occur in a fixed bed plug flow reactor. Data $\Delta H^{\circ}_{f\ 298K}$ of each component to determine ΔH_r at 298 K can be seen in Table 1. The value of $\Delta H^{\circ}_{r\ 298K}$ for the main reaction is obtained by:

$$\Delta H^{\circ}_{r\ 298K} = \sum \Delta H^{\circ}_{f\ 298K\ product} - \sum \Delta H^{\circ}_{f\ 298K\ reactant} \quad (6)$$
$$\Delta H^{\circ}_{r\ 298K} = \Delta H^{\circ}_{f\ 298K\ (CH3)2O} + \Delta H^{\circ}_{f\ 298K\ H2O} - 2\Delta H^{\circ}_{f\ 298K\ CH3OH}$$
$$\Delta H^{\circ}_{r\ 298K} = \big(-184.05 + (-241.83)\big) - \big(2 \times (-201.17)\big)\ kJ/mol$$
$$\Delta H^{\circ}_{r\ 298K} = -23.54\ kJ/mol$$

Based on the calculation, obtained $\Delta H^{\circ}_{r\ 298K}$ = -23.54 kJ/mol with negative value that indicates the reaction is exothermic.

Table 1. Enthalpy formation of compounds

Compounds	Molecular Formula	$\Delta H^{\circ}_{f\ 298K}$ (kJ/mol)
Methanol	CH_3OH	-201.17
Dimethyl ether	$(CH_3)_2O$	-184.05
Water	H_2O	-241.83

Data $\Delta G^{\circ}_{f\,298K}$ of each component to determine ΔG_r at 298 K can be seen in Table 2. The value of $\Delta G^{\circ}_{r\,298K}$ for the main reaction is obtained by:

$$\Delta G^{\circ}_{r\,298K} = \sum \Delta G^{\circ}_{f\,298K\,product} - \sum \Delta G^{\circ}_{f\,298K\,reactant} \quad (7)$$

$$\Delta G^{\circ}_{r\,298K} = \Delta G^{\circ}_{f\,298K\,(CH3)2O} + \Delta G^{\circ}_{f\,298K\,H2O} - \Delta G^{\circ}_{f\,298K\,CH3OH}$$

$$\Delta G^{\circ}_{r\,298K} = \left(-112.93 + (-228.59)\right) - \left(2 \times (-162.51)\right)\ kJ/mol$$

$$\Delta G^{\circ}_{r\,298K} = -16.48\ kJ/mol$$

Based on the calculation, obtained $\Delta G^{\circ}_{r\,298K}$ = -16.5 kJ/mol with a negative value that indicates the reaction is spontaneous. The value of equilibrium constant (I) at 298 K can be calculated by:

$$\ln K_{298} = \frac{-\Delta G^{\circ}_{r\,298K}}{RT} \quad (8)$$

$$\ln K_{298} = \frac{-(-164800\frac{J}{mol})}{8.314\frac{J}{mol.K}\times 298\ K}$$

$$\ln K_{298} = 6.652$$

$$K_{298} = 774.331$$

For reaction temperature 523.15 K, the equilibrium constant (*K*) can be calculated by:

$$\ln \frac{K_{523.15}}{K_{298}} = \frac{\Delta H^{\circ}_{r\,298K}}{R} \times \left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \quad (9)$$

$$\ln \frac{K_{523.15}}{774.331} = \frac{-23540\frac{J}{mol}}{8.314\frac{J}{mol.K}} \times \left(\frac{1}{523.15\ K} - \frac{1}{298\ K}\right)$$

$$\ln \frac{K_{523.15}}{774.331} = -4.0891$$

$$K_{523.15} = 12.9734$$

Table 2. Gibbs free energy formation of compounds

Compounds	Molecular Formula	$\Delta G^{\circ}_{f\,298K}$ (kJ/mol)
Methanol	CH_3OH	-162.51
Dimethyl ether	$(CH_3)_2O$	-112.93
Water	H_2O	-228.59

Based on the calculation, the equilibrium constant value of the reaction operates at 250 °C ($K_{523.15}$) = 12.9734, so the reaction is reversible.

2.3. Energy Optimization Method

In order to optimize energy in the production of dimethyl ether, it is necessary to make modifications in the process. In the initial base model, there are two heaters used to heat methanol to reach the reaction temperature before entering the reactor (R-100) as illustrated in process flow diagram of Figure 2 and represented in the ASPEN HYSYS simulation in Figure 3. Heat exchanger is a kind of utility unit that can have two functions, as heater and cooler [22], so that in chemical processes it can be used to increase energy use efficiency [23]. To maximize energy utilization, one of the heaters (H-100) can be replaced with a heat exchanger (HE-100) by using the high temperature reactor output stream to heat methanol as well as to cool the reactor output stream. On the other hand, the energy generated from the cooler (C-100) that is used to cool the reactor output stream can be used to energize the other heater (H-101). Thus, the energy of both heaters can be minimized.

The modification affects the temperature of the reactor output stream, which will be going through a separation process by distillation (T-100). The change affects the output temperature of the separated methanol. Therefore, the cooler (C-101) for cooling the recycled methanol stream is not required. The overall process modification reduces the total net energy in the dimethyl ether production process.

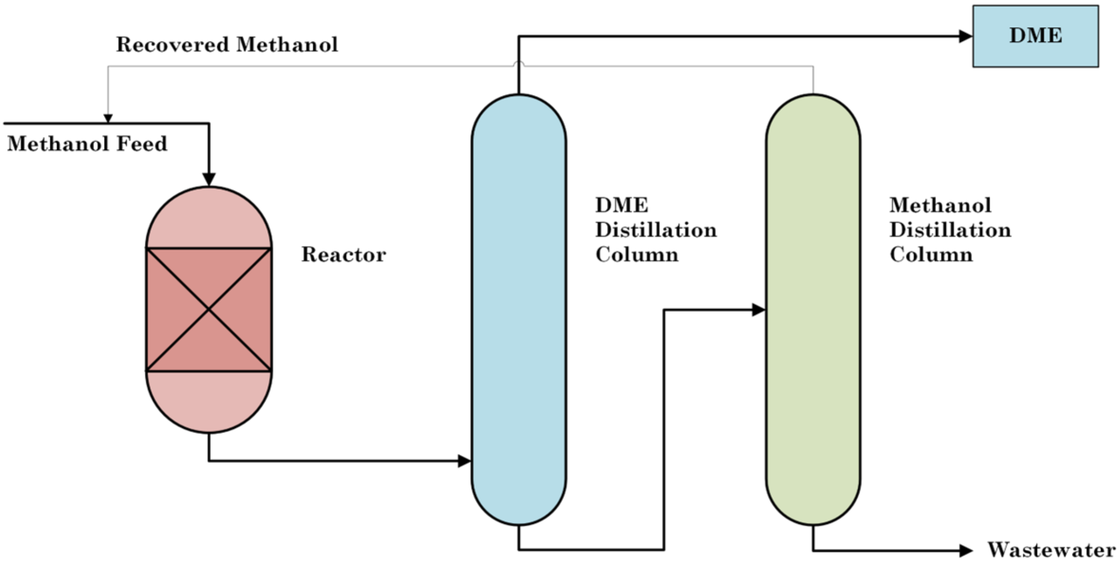

Figure 1. Block flow diagram of DME synthesis process from methanol dehydration [20]

3. Results and Discussion

3.1. Simplified Process Flow Diagram and Adjustments for Minimizing Net Energy Usage

The design production capacity of the Dimethyl Ether industrial plant as an example is 16,740 tonnes/year. The thermodynamic equation used in this flowsheet is NRTL-PR (Non-Random Two-Liquid Peng-Robinson). NRTL-PR is known to provide accurate results in predicting thermodynamic properties, especially for the gas phase and polar components at high pressures,

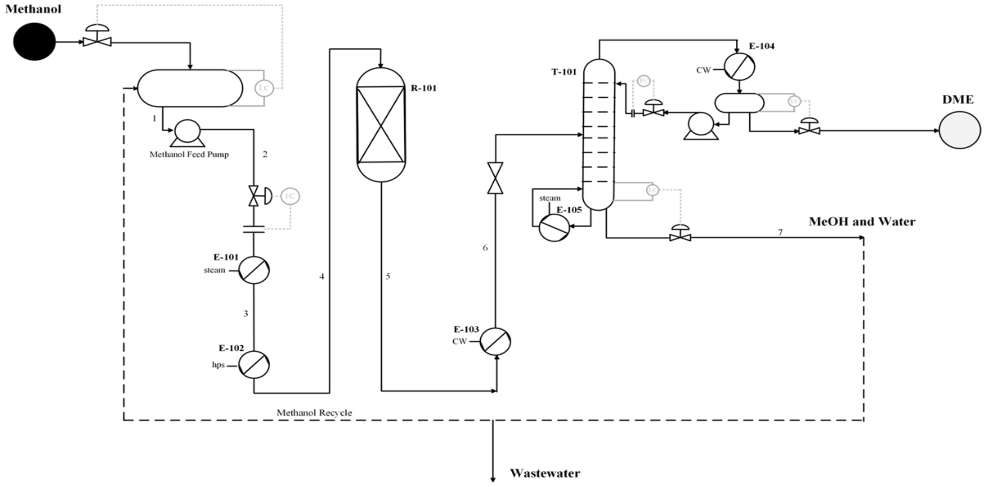

Figure 2. Process Flow Diagram (PFD) of basic process [20]

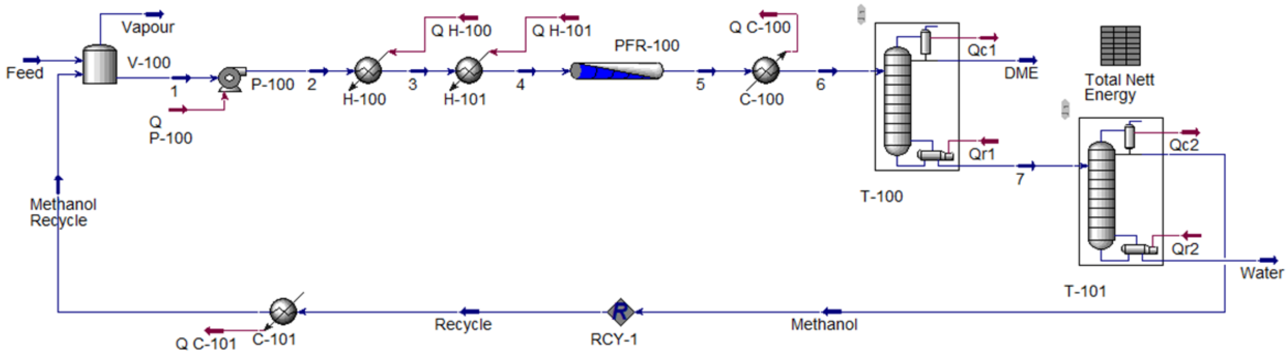

Figure 3. Aspen HYSYS simulation of basic process.

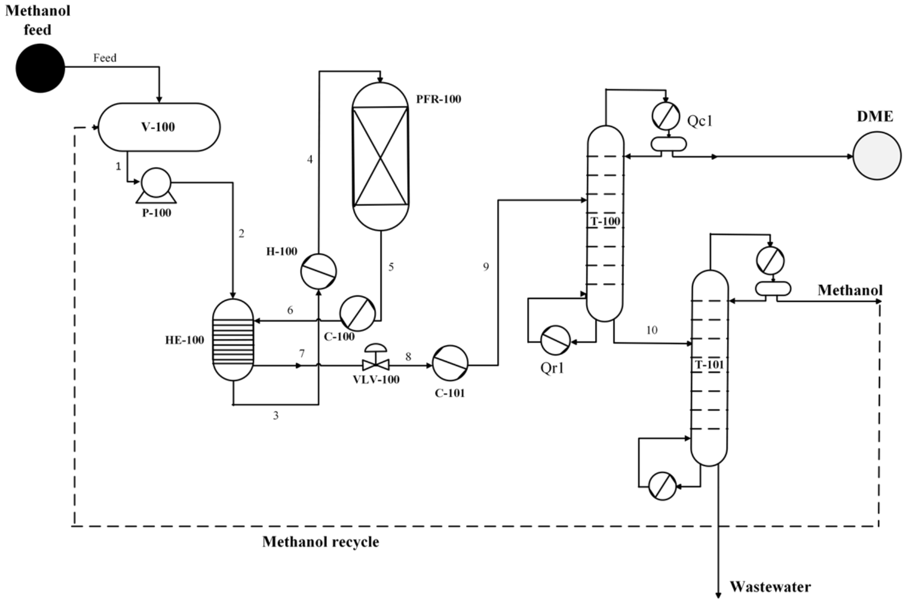

Figure 4. Process Flow Diagram (PFD) of modified process

above 1000 kPa [24]. The NRTL-PR fluid package is often relied upon in various industrial applications, especially in synthetic gas production units, due to its ability to handle complex mixtures involving polar and nonpolar molecular interactions. With the combination of the activity model NRTL for the liquid phase and the Peng-Robinson equation of state for the gas phase, this approach is the best choice in process simulations that require high accuracy at extreme pressure conditions [25].

The synthesis of DME from methanol dehydration reaction utilized a fixed bed plug flow reactor and γ-Al_2O_3catalyst was loaded due to its high selectivity and stability under reaction conditions [26]. The methanol input in this process is at 30 °C, 83.09 kgmol/h, and 0.997 atm from the methanol synthesis plant. Raw material (feed) is mixed with methanol recycle stream in the vessel (V-100). This mixture is increased in pressure using (P-100) to 10.86 atm and then heated using a heat exchanger (HE-100) and heater before entering the reactor (PFR-100). The reactor operates at 191.8°C and 32 atm pressure. After the dehydration process in the reactor, the components containing DME, H_2O, and unreacted CH_3OH are sent to a condenser (C-100) where it is partially liquefied. Then before entering the distillation, the pressure is lowered first with a control valve (VLV-100) routed to a secondary cooler (C-101) and then entered into the first distillation tower. DME will be obtained as the top product at (T-100) with a purity of 99.95% (molar basis). The bottom product at (T-100) is continued to the second distillation process (T-101) to separate unreacted and water. Unreacted methanol is recycled back into the process (stream 10) to maximize efficiency, while water is removed as wastewater. The modified process flow diagram of methanol dehydration reaction is shown in Figure 4, while mass and energy balances is shown in Table S1 (Supporting Information).

Modifications are made by replacing the heater or cooler with a heat exchanger to increase the energy efficiency presented in Figure 5. The chemical reaction in the PFR-100 reactor is an exothermic reaction, in which its heat energy can be used as a heat source in the heat exchanger for the pre-heater process before entering the reactor.

3.2. Evaluation of Net Energy Consumption of Modified Process

In this study, the heat transfer unit of the process was modified by changing the heater to heat exchangers (HE-100) and utilizing the energy generated from the cooler (C-100) as energy for the heater (H-100). The results of the total net energy can be seen in Tables 3 and 4.

Table 3. Total net energy of overall process

Energy stream	Basic process energy (kJ/h)	Modified process energy (kJ/h)
QP-100	5461	5357
QH-100	1.194e+006	-
QH-101	3.256e+006	-
QC-100	4.109e+006	-
QC-101	9.602e+004	3.981e+005
QHE-100	-	3.113e+006
Qc1	-1.381e+006	-1.527e+006
Qr1	1.273e+006	9.345e+005
Qc2	-9.785e+005	-5.207e+005
Qr2	9.738e+005	5.166e+005
Total	8.542e+006	2.921e+006

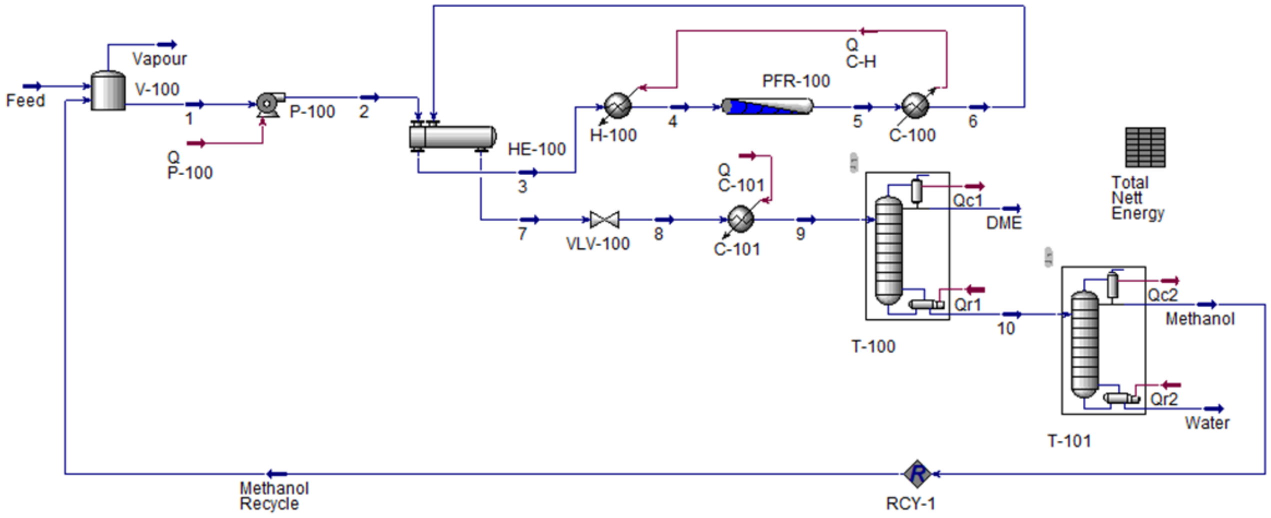

Figure 5. Aspen HYSYS simulation of modified process

3.2.1 Cooler energy utilization effect

The reactor output stream has a high temperature, reaching more than 300 °C. This stream needs to be cooled with a cooler (C-100) to 100 °C. The cooling process generates energy that can be used to heat the reactor inlet stream in the heater (H-100) to 191.8 °C, which is sufficient for the methanol dehydration reaction to take place in the reactor (R-100). Hence, the heater (H-100) does not require additional energy outside the existing process. As a result, energy consumption can be reduced. It can be seen in Table 4 that the heat energy generated by the cooler (QC-100) and that required by the heater (QH-100) is eliminated.

3.2.2 Heat exchanger addition effect

The addition of a heat exchanger (HE-100) plays a crucial role in enhancing energy efficiency [27]. The stream from cooler (C-100) has a temperature of 100 °C so that it can be utilized for heating fluid in the heat exchanger (HE-100) to heat up methanol feed before entering the reactor. Heat exchange occurs from the hot fluid at 100 °C to the cold methanol feed 33.7 °C, resulting in an increase in the methanol feed temperature to 141.6 °C, which is close to the reaction temperature. In addition, the use of heat exchanger (HE-100) can also reduce the workload of the heater (H-100) to achieve the optimal reaction temperature of 191.8°C. Table 4 shows that the use of heat exchanger (HE-100) itself can increase energy efficiency compared to using H-100 and H-101 combined.

Table 4. Heat flow comparison of heater unit

Energy Stream	Heater (H-100 & H-101)	Heat Exchanger (HE-100)
Heat flow (kJ/h)	4.45e+006	3.113e+006

4. Conclusion

This study successfully optimized the DME production process from methanol dehydration by employing energy integration strategies. The modifications, including replacing heaters with heat exchangers and utilizing excess energy from the cooling processes, resulted in a significant reduction 65.8% in net energy consumption from 8.54×10^6 kJ/h to 2.92×10^6 kJ/h total net energy consumption. By leveraging Aspen HYSYS simulations, the proposed design achieved high process efficiency while maintaining the target DME purity of 99.95%. These findings emphasize the critical role of energy optimization in industrial chemical processes, offering a sustainable and economically viable pathway for scaling up DME production. Future work could explore advanced catalyst formulations and further integration with renewable energy sources to maximize sustainability.

CRediT Author Statement

A.F. Ghoffaru: Conceptualization, Methodology, Investigation, Software, Visualization, Writing, Review & Editing, Supervision; J.L. Grasia: Conceptualization, Methodology, Visualization, Writing, Review & Editing, Project Administration, Validation; A.A. Wijaya: Conceptualization, Methodology, Formal Analysis, Resources, Validation, Writing; N.D. Ramadhan: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing; A.N. Saputro: Data Curation, Writing; A. Maharani: Formal Analysis, Writing. All authors have read and agreed to the published version of the manuscript.

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