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Research Article

Enhancing Methanol Production from Syngas through Heat Exchanger Modification and Vapour Distillate Flow Optimization

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Abstract

Methanol production from syngas represents a promising route to strengthen energy independence and reduce reliance on imports. Conventional processes, however, are constrained by low per-pass conversion and unstable reactor inlet conditions, which limit efficiency and accelerate catalyst deactivation. This study investigates process modifications, focusing on two key strategies: the addition of a heat exchanger to stabilize and elevate reactor inlet temperatures, and the optimization of vapor distillate flow in the distillation column to enhance product purity. The modified process achieved a substantial improvement in methanol conversion, rising from 28.34% in the base configuration to 98.70%, while product purity increased from 97.68% to 98.95%. The heat exchanger ensured better thermal conditioning of recycle streams, reducing temperature fluctuations and improving reaction stability, whereas distillate flow optimization enhanced separation efficiency by balancing vapor and liquid reflux. These results demonstrate that targeted retrofitting of existing plants can deliver significant gains in efficiency, stability, and sustainability without the need for new construction.

Keywords: Methanol; Syngas; Heat; Distillation; Simulation

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1. Introduction

In recent decades, global energy demand has risen sharply alongside population growth and industrial expansion, while the limitations of fossil fuel resources and increasing consumption have contributed significantly to energy crises, declining air quality, global warming, and rising greenhouse gas emissions [1]. This situation underscores the urgent need for green energy sources such as methanol [2]. Methanol (CH_3OH), the simplest alcohol, is a light, colorless, volatile, flammable, and toxic liquid with a distinctive odor, widely used as a solvent, antifreeze, fuel, and as a feedstock in industries producing acetic acid, formaldehyde, MTBE, polyvinyl, polyester, and DME [3].

Methanol can theoretically be produced from biomass distillation, coal gasification, or natural gas synthesis. However, Indonesia's abundant natural gas reserves offer a strategic feedstock option, with national production reaching 2,420,059.5 MMscf in 2023 [4]. The availability of natural gas, combined with rising industrial demand, highlights the promising prospects of expanding domestic methanol production, particularly as Indonesia continues to rely on imports. Syngas derived from natural gas, composed mainly of H_2, CO, and CO_2, provides a simpler conversion pathway with lower energy consumption, operating costs, and capital investment compared to direct natural gas

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processing, while also reducing catalyst poisoning due to lower impurity levels [5].

Nevertheless, syngas-based methanol production faces technical challenges, notably low per-pass conversion limited by reactor thermodynamics, which conventional plants address through large recycle loops that increase energy use and compression loads. Furthermore, mixing recycled streams with fresh syngas often causes temperature instability at the reactor inlet, reducing conversion efficiency, triggering hotspots, and accelerating catalyst deactivation [6]. To address these issues, process modifications such as heat recovery, temperature control, and selective product separation, combined with flow optimization, can significantly improve efficiency compared to conventional approaches [7].

This study therefore aims to enhance methanol synthesis performance by adjusting reactor inlet stream temperatures through optimized mixing and heat exchangers, and by improving product purity via distillation column flow optimization. These strategies are expected to deliver a more efficient, stable, and economically viable process without requiring new plant construction, offering a practical solution to meet Indonesia's growing methanol demand while integrating thermodynamics, kinetics, heat and mass transfer, and process systems analysis into a comprehensive framework for sustainable production.

2. Methods

2.1 Process Simulators Used for Evaluation

Process simulation has become an indispensable tool in process engineering, facilitating improved system control, maintenance strategies, and decision-making in response to operational challenges, regulatory requirements, and market competition. In recent years, simulation software has exerted a significant influence on chemical engineering (ChE) curricula, serving as a powerful instrument for the design, analysis, and operation of chemical plants. Prominent commercial simulators include Aspen Plus, Aspen HYSYS, Unisim, VMGSim, ProMax, and ChemCad. These platforms are capable of addressing complex engineering problems and enable chemical engineers to perform rapid, high-level calculations. These robust software packages can handle complex engineering tasks and allow chemical engineers to perform rapid and sophisticated calculations. Particularly, Aspen HYSYS is a process simulator widely used at an industrial level, especially for performing the conceptual design, control, optimization, and process monitoring in different stages of any project [8].

Aspen HYSYS is used as an integrated process simulator in both steady-state and dynamic modes. The simulation models created in HYSYS are utilized for plant design, performance monitoring, problem-solving, operational process improvement, business planning, and asset management. The software offers an integrated set of intuitive and interactive tools for simulation and analysis, as well as real-time applications. It provides rapid evaluations of safe and reliable designs through the quick creation of interactive models for "what-if" studies and sensitivity analyses [9]. In the simulation process for methanol production from syngas, the Non-Random Two-Liquids (NRTL) property package was used for optimization. The NRTL model is designed to handle mixtures where components interact non-ideally, such as those exhibiting partial miscibility, azeotropy, or strong molecular interactions. It is effective for vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), and vapor-liquid-liquid equilibrium (VLLE) calculations in both binary and multicomponent systems [10]. This is particularly relevant to methanol synthesis, where the process involves highly non-ideal methanol-water mixtures and the partial solubility of light gases such as CO, CO_2, and H_2.

2.2. Process Description

Methanol (CH_3OH) is the simplest alcohol, consisting of one carbon, one oxygen, and four hydrogen atoms. Methanol is one of the most important raw materials in the chemical industry for producing formaldehyde, acetic acid, methyl formate, etc. It has also been used as fuel for methanol automobiles. Global methanol production has increased annually, and the demand is still rising. Commercial methanol is predominantly synthesized from syngas, a gas mixture typically derived from the reforming of fossil fuels or renewable feedstocks [11].

Methanol synthesis from syngas proceeds through several reactions, primarily CO hydrogenation, CO_2 hydrogenation, and the water-gas shift reaction. Based on the stoichiometric reactions of methanol synthesis, the syngas composition plays a crucial role in determining methanol yield. Both product composition and feedstock conversion under equilibrium conditions are strongly dependent on the initial composition of the feed. According to Iyer *et al.* [12], a thermodynamic equilibrium model was used to evaluate how feed composition affects methanol synthesis under isothermal and adiabatic conditions, considering both single- and two-phase operation. Their results indicate that under isothermal single-phase conditions, CO conversion increased with an increase in CO/H_2

ratio and decreased with an increase in CO_2/H_2 ratio. For adiabatic operation, they found the reactor outlet temperature was higher than the inlet temperature and it increased with an increase in CO/H_2 ratio.

The stoichiometric reactions involved in methanol synthesis using syngas as feedstock are:

$$CO + 2H_2 \rightleftharpoons CH_3OH, \Delta H_{298K} = -90.7\ kJ \cdot mol^{-1} \quad (1)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O, \Delta H_{298K} = -49.51\ kJ \cdot mol^{-1} \quad (2)$$

From Eq. (1), CO reacts with H_2 to form methanol. From Eq. (2), CO_2 reacts with H_2 to form methanol with water as a side product. Additionally, the reverse water gas shift (RWGS) reaction [13] could also take place,

$$H_2 + CO_2 \rightleftharpoons CO + H_2O, \Delta H_{298K} = -41.19\ kJ \cdot mol^{-1} \quad (3)$$

These reactions are reversible and limited by thermodynamic equilibrium. Both CO and CO_2 hydrogenation reactions are exothermic and involve a reduction in the total number of moles; therefore, low temperatures and high pressures thermodynamically favor methanol formation, following Le Chatelier's principle. In contrast, the RWGS reaction is endothermic and proceeds with no change in the number of moles [11].

2.3. Method to Improve Net Energy Efficiency of Methanol Production

In industrial operations, energy represents a fundamental and indispensable resource, as nearly all processes depend on continuous energy input. Several studies have focused on the energy utilization efficiency of the syngas-to-methanol process because of its high energy consumption. For example, a hybrid methanol purification process was developed to improve energy efficiency, which combined heat pump distillation and double-effect thermal integration by designing an intermediate heater to shunt the heat load of the reboiler. Although this strategy can reduce energy consumption of certain subprocesses in the syngas to methanol process, it has complicated thermal-integration requirements and exhibits limited operational flexibility when feed composition or process conditions fluctuate [14]. Therefore, other energy-saving strategies are required to achieve efficiency improvements throughout the entire process.

The integration of heat exchanger networks (HENs) could lead to a comprehensive heat exchange strategy for the entire syngas to methanol process by considering energy utilization, energy efficiency, operation cost, and equipment cost. Energy consumption can be reduced by using an optimized heat exchange strategy [15]. According to Putri et al. [16] adding heat exchanger for process stream heat recovery can reduce total energy consumption by up to 58.5% in methanol synthesis plants, while also increasing methanol yield from 97.47% to 99%. Not only that, optimizing flow parameters in distillation columns is also a highly effective strategy for enhancing product purity in methanol. Increasing the reflux ratio generally leads to higher product purity, as more condensed vapor is returned to the column, improving separation. The study conducted by Fitriah and Sari [17] demonstrated that optimizing the reflux ratio in the distillation column can achieve product purity of up to 85%. Therefore, the integration of additional heat exchangers serves to improve energy efficiency, whereas optimizing distillate flow parameters in the distillation column is essential for enhancing final methanol purity.

3. Results and Discussion

3.1. Comparison Between Basic and Modified Process

The simulation of methanol production from syngas, covering both the basic and modified processes, is illustrated in Figures 1-4 using Aspen HYSYS. The process flow diagram (PFD) for the basic configuration is shown in Figure 1, with its corresponding simulation presented in Figure 2. In the modified process, illustrated in Figures 3 and 4, an additional heat exchanger (HE-105) is installed before the stream enters MIX-02. This modification ensures that the recycle stream is thermally conditioned prior to mixing, thereby enhancing temperature control and improving overall process stability.

3.2. Thermodynamics Review

To determine whether the reaction is exothermic or endothermic, and to evaluate its reversibility, the standard heat of reaction

Table 1. The value of $\Delta H_f°$ and $\Delta G_f°$ of compounds.

Components	Molecular Formula	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)
Carbon Dioxide	CO_2	-393.51	-394.4
Carbon Monoxide	CO	-110.54	-137.2
Methanol	CH_3O	-201.17	-162.2
Water	H_2O	-241.8	-228.6
Nitrogen	N_2	0	0
Hydrogen	H_2	0	0

(ΔH^{o}_{298K}) at 1 bar and 298 K must be calculated from the standard heats of formation of the reactants and products. The corresponding values of ΔH_f° and ΔG_f° for each compound are provided in Table 1.

Standard heat for each reaction is calculated as follow based on the Table 1:

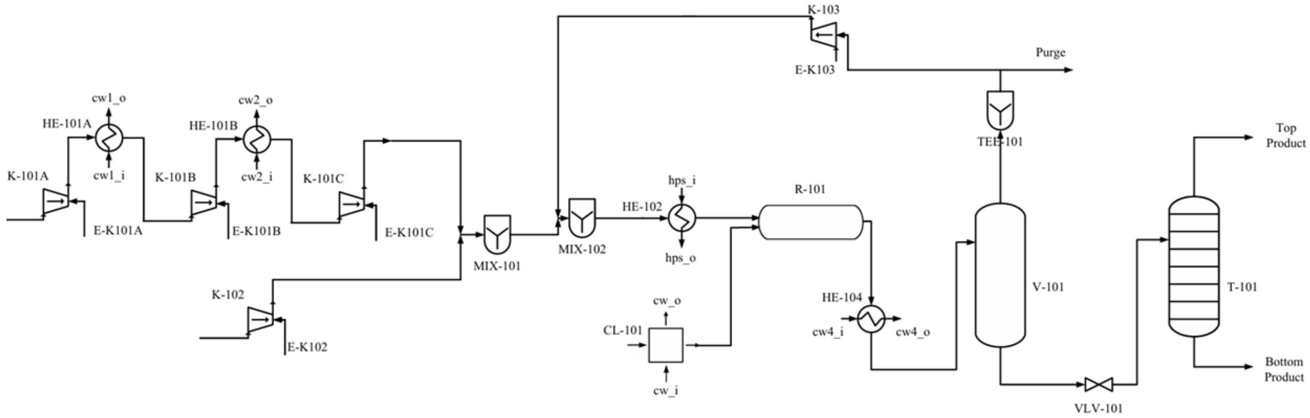

Figure 1. Process Flow Diagram (PFD) of basic (unmodified) process.

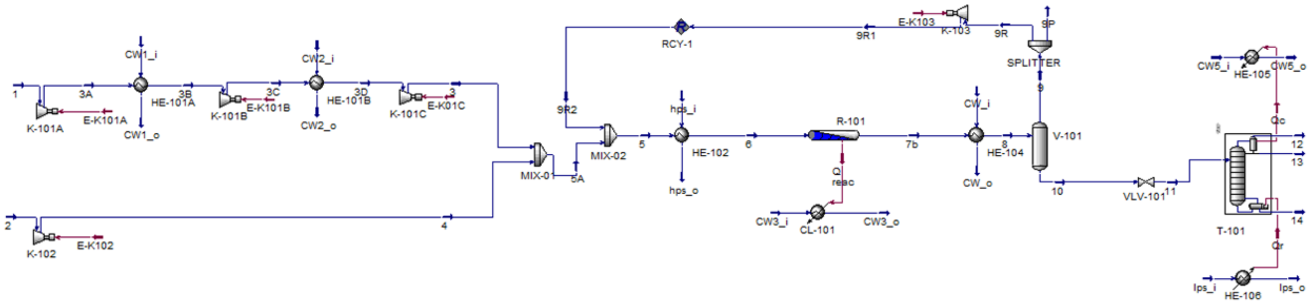

Figure 2. Aspen HYSYS simulation of basic (unmodified) process.

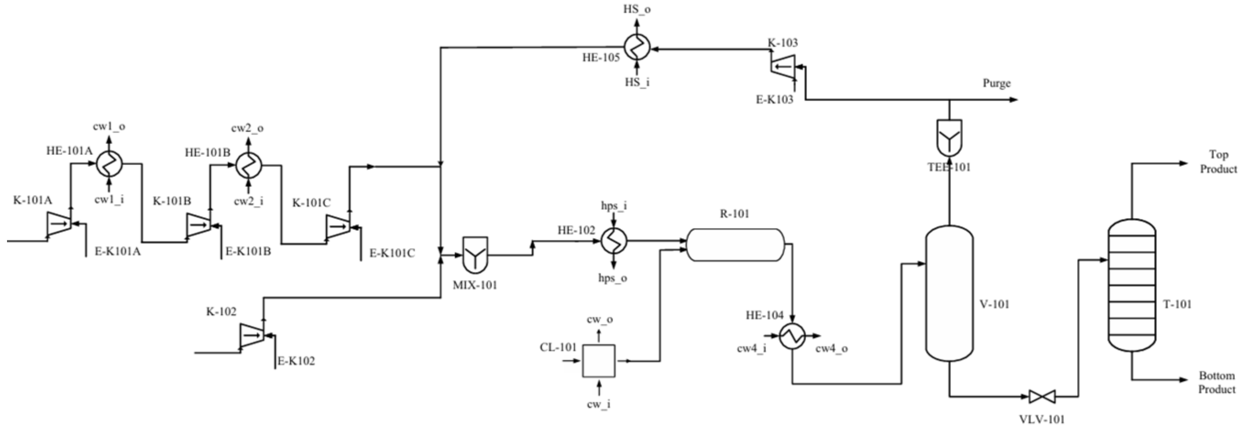

Figure 3. Process Flow Diagram (PFD) of modified process.

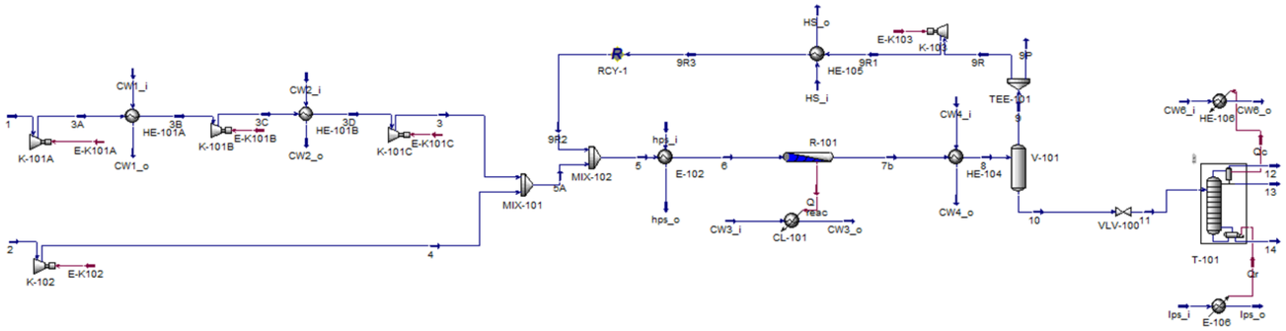

Figure 4. Aspen HYSYS simulation of modified process.

$$\Delta H^{\circ}_{298K} = \sum \Delta H^{\circ}_{f} \text{ product} - \sum \Delta H^{\circ}_{f} \text{ reactan}$$

(1) $CO + 2\,H_2 \rightleftharpoons CH_3OH$

$$\Delta H^{\circ}_{298K} = -90.63\,\frac{kJ}{mol}$$

(2) $CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O$

$$\Delta H^{\circ}_{298K} = -49.46\,\frac{kJ}{mol}$$

(3) $CO + H_2O \rightleftharpoons CO_2 + H_2$

$$\Delta H^{\circ}_{298K} = -41.17\,\frac{kJ}{mol}$$

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

$$\Delta H_{\text{total reaction}} = -180.8\,\frac{kJ}{mol}$$

Based on the calculations, we get the value $\Delta H_{\text{total reaction}} = -180.8$ kJ/mol, which is a negative value so that the reaction is exothermic.
Gibbs energy was calculated as follow:

$$CO + 2\,H_2 \rightleftharpoons CH_3OH \qquad (1)$$

$$\Delta G^{0}_{f298} = \Delta G_{\text{f product}} - \Delta G_{\text{f reactant}} = -25000\,\frac{J}{mol}$$

$$\ln K_{298} = \frac{\Delta G^{0}_{f298}}{-R\,T}$$

$$K_{298} = 2.4113 \times 10^{4}$$

At operating temperature of 170 °C (443.15 K):

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

$$K_{443.15} = 2.3470 \times 10^{4}$$

$$\ln K_{443.15} = \frac{\Delta G^{0}_{f443.15}}{-R\,T}$$

$$\Delta G^{0}_{f443.15} = -37077.40\,\frac{J}{mol}$$

Because the value of $K_{443.15} > 1$, the first (main) reaction is reversible. A small equilibrium constant indicates that equilibrium is reached when only a limited proportion of the reactants are converted into products.

Calculation of ΔG^{0}_{298} reaction (2):
$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O$

$$\Delta G^{0}_{298} = \Delta G_{\text{f product}} - \Delta G_{\text{f reactant}} = 3580\,\frac{J}{mol}$$

$$\ln K_{298} = \frac{\Delta G^{0}_{f298}}{-R\,T}\ ;\ K_{298} = 0.2358$$

At operating temperature of 170 °C (443.15 K):

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

$$K_{443.15} = 0.2323$$

$$\ln K_{443.15} = \frac{\Delta G^{0}_{443.15}}{-R\,T}$$

$$\Delta G^{0}_{443.15} = 5378.11\,\frac{J}{mol}$$

Because the value of $K_{443.15} < 1$, thus, the second reaction is reversible.

Calculation of ΔG^{o} reaction (3):
$CO + H_2O \rightleftharpoons CO_2 + H_2$

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

$$\Delta G_{\text{reaction}} = -28580\,\frac{J}{mol}$$

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

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

$$K_{298} = 1.02282 \times 10^{5}$$

At operating temperature of 170°C (443.15 K):

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

$$K_{443.15} = 1.01033 \times 10^{5}$$

$$\ln K_{443.15} = \frac{\Delta G^{0}_{443.15}}{-R\,T}$$

$$\Delta G^{0}_{443.15} = -42455.51\,\frac{J}{mol}$$

Because the value of $K_{443.15} > 1$, thus, the third reaction is irreversible.

3.3. Heat Exchanger Modification for Conversion Enhancement

The conversion efficiency of methanol synthesis rises with increasing temperature until an optimum point is reached. In the case of CO_2 hydrogenation to methanol, the best operating conditions are achieved at elevated temperatures (up to 300 °C) and high pressures (5–10 MPa) [5]. To reach the required temperature, the reactor inlet stream is regulated using a heat exchanger (HE). The HE is integrated into the process to facilitate heat transfer between two streams, enabling the recovery of waste heat from one stream to warm another, thereby reducing the need for external heating or cooling [6]. When streams at different temperatures are mixed, the resulting stream attains an intermediate temperature, as the temperature difference drives heat transfer until equilibrium is established [7]. Thus, in the simulated process, the reactor inlet temperature can be raised by adjusting the mixing of streams to minimize temperature differences.

In the base configuration, a reactor inlet temperature of 101.4 °C is achieved by mixing stream 9R2 at 89.36 °C with stream 5A at 140 °C. In the modified configuration, mixing stream 9R2 at 102 °C with stream 5A at 140 °C produces an inlet temperature of 111.1 °C. In both cases, the mixed streams are subsequently heated in the HE before entering the reactor, resulting in final inlet temperatures of 102 °C for the base process and 170 °C for the modified process.

3.4 Purity Improvement by Distillate and Flow Rate Optimization

One key factor affecting the separation efficiency of a distillation column is the condensation of the overhead product. When very light compounds are present in the mixture, a partial condenser is used. Since these compounds require either high pressures or extremely low temperatures for complete condensation, the energy demand for total condensation becomes substantial [18].

In a distillation column equipped with a partial condenser, separation efficiency can be controlled by adjusting both the vapor distillate and liquid distillate flow rates. Increasing the vapor distillate flow rate enhances the removal of light components through the vapor phase, thereby improving the methanol purity of the distillate [19]. In contrast, a higher uncondensed distillate flow rate reduces the amount of condensate formed. With less distillate condensed, the reflux flow decreases, weakening liquid–vapor contact. This reduction in contact lowers the extent of component separation and ultimately diminishes distillate purity [17].

Therefore, optimizing the distillate and vapor distillate flow rates is essential to achieve high methanol purity. This optimization is performed using the HYSYS optimizer, where the independent variables are the molar flow rates of the distillate and vapor distillate, and the dependent variable is the methanol mole fraction in the distillate.

3.5. Analysis of Conversion and Purity Between Basic and Modified Process

The addition of a heat exchanger before the mixer unit has a significant impact on the reaction performance in the methanol synthesis process from syngas. The heat exchanger functions to reduce the temperature difference between the feed streams prior to entering the reactor, thereby producing feed conditions with a higher temperature. Temperature homogeneity is crucial because methanol synthesis occurs on the catalyst surface, and the stability of the initial feed conditions strongly influences adsorption effectiveness and reaction rate. Simulation results in Figure 5 demonstrate that the modified process achieves a higher conversion compared to the base process. This improvement is not only attributed to a more uniform heat distribution but also to the increased initial reaction rate resulting from the higher feed temperature [20]. Consequently, the system reaches a reaction state closer to equilibrium more rapidly, and the rate of equilibrium attainment contributes to enhancing the overall conversion without contradicting the equilibrium constant, which remains unchanged under isothermal conditions.

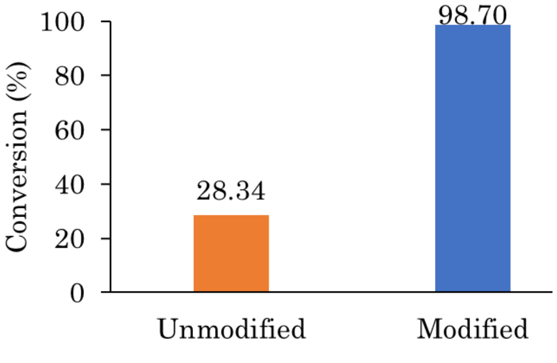

Figure 5. Comparison of methanol conversion in the base and modified processes.

In addition to conversion, the analysis also examined changes in product purity through the optimization of vapor distillate and liquid distillate flow rates in the separation unit. Variations in these flow rates directly affect the distribution of components within the column, thereby influencing the purity of the methanol produced. A lower vapor distillate flow rate increases the amount of condensate returned to the distillation column, which enhances the opportunity for liquid–vapor contact and consequently improves separation efficiency [11]. The optimization results presented in Table 2 demonstrate a clear relationship between the vapor distillate and distillate flow rates and the final product purity. Increasing the vapor distillate flow rate generally facilitates the removal of light components and non-condensable gases, thereby raising the methanol fraction in the distillate. The optimization results confirm that higher vapor distillate flow rates lead to improved methanol purity. Therefore, balancing these two flow rates is a critical factor in achieving optimum methanol purity. Overall, the comparison between the base and modified processes shows that improving feed conditions and regulating separation flow distribution significantly contribute to achieving higher conversion and product purity.

4. Conclusion

The process modifications evaluated in this study, namely the integration of an additional heat exchanger prior to the mixing unit and the optimization of vapor distillate flow in the distillation column, proved highly effective in enhancing methanol synthesis from syngas. The heat exchanger improved thermal conditioning of recycle streams, resulting in higher and more

Table 2. Comparison of methanol purity in the base and modified processes.

Process	Vapor distillate flow rate (kmol/jam)	Distillate flow rate (kmol/jam)	Methanol purity (%)
Basic	8.288	780.7	97.68
Modified	4.144	780.5	98.95

stable reactor inlet temperatures that accelerated reaction rates and increased conversion from 28.34% to 98.70%. In parallel, optimization of distillate flow parameters enhanced separation efficiency, raising methanol purity from 97.68% to 98.95%. These improvements demonstrate that targeted retrofitting of existing plants can significantly boost efficiency, stability, and product quality without the need for new construction. Overall, the findings confirm that combining heat recovery strategies with separation flow optimization provides a practical, economically viable, and environmentally sustainable approach to advance methanol production.

CRedit Author Statement

Author Contributions: D. D. S. Astuti: Writing – review & editing, Writing – original draft, Writing – Results and Discussion, Supervision, Resources, Conceptualization, Investigation, Formal Analysis, Project Administration, PFD (Microsoft Visio); A. Mu'amar: Writing – Results and Discussion, Conceptualization, Investigation, Formal Analysis, Conceptualization, Simulation (ASPEN Hysys) ; A. T. P. S: Writing – Abstract and Conclusion), Writing – review & editing; A. Maizalfania: Writing, Methodology; A. R. Dewi: Writing, Introduction; S. Nurrahim: Validation Data Curation. All authors have read and agreed to the published version of the manuscript.

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