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Research Article

Process Optimization for Enhanced Dimethyl Ether Yield through Methanol Synthesis and Dehydration of Syngas-Derived Methanol

Gayuh Tahta Aditama Nugraha*, Fardan Akbar Maulana, Muhammad Erlangga Pratama, Muhammad Hamim Safrudin, Fauzan Aqil Afdika

Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang 50275, Indonesia.

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Abstract

The global energy crisis and continued reliance on fossil fuels highlight the urgent need for sustainable alternatives. Dimethyl ether (DME) has emerged as a promising low carbon fuel owing to its clean combustion properties and versatility as an LPG substitute, diesel replacement, and chemical feedstock. This study focuses on optimizing the design of DME production from syngas derived methanol, with particular emphasis on conversion efficiency and thermal management. Base case simulations revealed that higher methanol dehydration conversion elevated reactor temperatures by nearly 100 °C, thereby disrupting equilibrium and hindering effective separation. To address these challenges, a modified process integrating cooling, heating, and distillation units was developed, achieving an 80% conversion and a DME yield of 97.6%, while simultaneously reducing excessive cooling requirements. These findings demonstrate that improved thermal control and separation strategies can significantly enhance both energy efficiency and environmental performance, reinforcing DME's potential role in the transition toward cleaner energy systems.

Keywords: Dimethyl ether (DME); Methanol dehydration; Process optimization; Sustainable production

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1. Introduction

The global energy crisis, coupled with the rising consumption of fossil fuels, underscores the urgent need to transition toward cleaner and more sustainable energy sources. Persistent reliance on oil, natural gas, and coal exerts severe pressure on the environment, primarily through greenhouse gas emissions and harmful air pollutants [1]. This challenge is further intensified by volatile fossil fuel prices and the finite nature of long-term reserves, reinforcing the necessity for safe, stable, and environmentally friendly energy alternatives [2].

Dimethyl ether (DME) is a simple ether compound with the chemical formula CH_3OCH_3 that is gaining significant attention as a clean and sustainable alternative fuel due to its favorable physical and chemical properties, which support its use as an LPG substitute, clean diesel fuel, and chemical industry feedstock [3,4]. Its combustion produces markedly lower emissions of particulates, sulfur oxides, nitrogen oxides, and greenhouse gases compared to conventional fossil fuels, making DME an important candidate in the transition to low-carbon energy [3,5]. DME can also be produced sustainably from hydrogen and captured CO_2, enabling a reduction in greenhouse gas emissions by approximately 82–86% relative to petroleum-based fuels, although the production stage still contributes the most to its overall environmental impact [6]. Additionally, its non-toxic nature and low-pressure liquefaction characteristics simplify storage and distribution processes [7]. Globally, the development of DME as an energy source has progressed with varying priorities, for example, in China, large-scale production is carried out from coal-based

* Corresponding Author.
Email: gayuhtahtaaditaman@students.undip.ac.id (G. T. A. Nugraha)

methanol, and DME is commonly blended with LPG, typically below 20% to ensure compatibility with existing infrastructure for cooking and heating applications [8].

Dimethyl ether (DME) is typically produced through the dehydration of methanol in a fixed-bed reactor. To ensure a cleaner process, the methanol used is derived from syngas obtained via gasification of non-fossil solid fuels. This syngas originates from biomass gasification, where the ultimate components of biomass decompose into CO and H_2, collectively known as syngas. Syngas is widely utilized as a feedstock for the synthesis of various compounds such as methanol, DME, polypropylene, and diverse hydrocarbons [9]. In the DME production process, the gasification-derived syngas is first converted into methanol at 225 °C and 45–50 atm using a Cu/ZnO catalyst, according to the following reaction [9]:

$$CO + 2H_2 \rightarrow CH_3OH \quad \Delta H°_{298} = -91.0 \text{ kJ/mol} \qquad (1)$$

The methanol produced is then fed into a fixed-bed dehydration reactor at 260 °C and 15–20 atm with an Al_2O_3 catalyst. Under these conditions, methanol undergoes dehydration to form DME via the reaction [9]:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad \Delta H°_{298} = -12.0 \text{ kJ/mol} \qquad (2)$$

Methanol dehydration is a reversible, exothermic reaction that proceeds without any change in the total number of moles. Consequently, operating pressure does not affect the equilibrium conversion. However, selecting a lower reaction temperature provides thermodynamic advantages by enhancing DME formation. This dehydration reaction occurs with the aid of acidic catalysts [10].

To enhance the production of Dimethyl Ether (DME) from both economic and operational perspectives, this study explores the design of a DME plant through simulations that prioritize conversion improvement. The main limitation of the current process lies in the conversion rate, which remains at 75%. Increasing the conversion further is constrained, as higher conversion levels lead to a significant rise in outlet temperature. Simulation results using HYSYS indicate that at a 90% conversion rate, the outlet temperature can increase by approximately 100 °C. To address this issue, the proposed solution involves the addition of a cooling unit to maintain thermal conditions within safe limits. This cooling system ensures that when the stream enters the separator, the temperature remains within the appropriate range, below the boiling point of DME but still above the boiling points of other components such as hydrogen, methanol, and related compounds. Optimizing energy utilization is not only crucial for improving industrial performance but also aligns with broader sustainability goals within the industrial sector.

Based on research on enhancing Dimethyl Ether (DME) production, this study focuses on designing a plant that is both economically and operationally efficient through conversion-improvement simulations combined with thermal control. The primary objective is to achieve higher conversion levels without compromising the stability of outlet temperatures, thereby ensuring that the process remains safe and optimal. The addition of a cooling unit has proven to be an effective solution for maintaining thermal conditions in accordance with the boiling characteristics of DME and other involved components. Consequently, this study not only offers strategies to improve industrial performance but also provides a more sustainable approach to DME production.

2. Methods

The production process model for DME from the dehydration of methanol derived from syngas was developed using Aspen HYSYS V11, incorporating the components dimethyl ether, CO, hydrogen, H_2O, and methanol. The fluid package applied in this simulation was NRTL (Non-Random Two-Liquid). NRTL was selected due to its proven capability to accurately represent non-ideal interactions between liquid and gas phases in multicomponent systems. This model is particularly well-suited for analyzing phase equilibrium and thermodynamic properties in the separation of DME and methanol, which are the primary constituents in DME synthesis from syngas. Its effectiveness is most evident under conditions where the mixture demonstrates non-ideal behavior [11].

To improve the yield of DME, the production process was modified by incorporating a cooler, valve, heater, and distillation column, along with an increase in reactor conversion. This modification was necessary because the initial process achieved only 75% conversion. Increasing the conversion to 90% caused the outlet temperature to rise by approximately 100 °C. Therefore, a cooler was introduced to ensure that the stream entering the separator remained under optimal conditions, specifically below the boiling point of DME but above the boiling points of syngas components. The boiling point of DME is −24.8 °C, while those of hydrogen and carbon monoxide are −252.88 °C and −191.5 °C, respectively [12-14]. This modification substantially enhances the conversion efficiency

of DME formation, and the yield of DME can be determined using Equation (1) [10]:

$$DME\ global\ yield\ (\%) = \frac{moles\ of\ DME\ produced \times 2}{moles\ of\ CO\ and\ CO_2 in\ the\ clean\ syngas} \times 100\% \quad (1)$$

3. Results and Discussion

3.1. Process Description of Basic Process Before Process Modification

The production of dimethyl ether (DME) is carried out through two main reaction stages, namely the formation of methanol from syngas and the subsequent dehydration of methanol to produce DME (Figure 1). The process simulation was conducted using Aspen HYSYS V12 with the NRTL–Ideal fluid package, selected due to its suitability for modeling non-ideal gas–liquid systems involving methanol, water, DME, and syngas components. The feed syngas consists of CO and H_2 with mole fractions of 0.3 and 0.7, respectively, introduced into the system at a temperature of 225 °C and a pressure of 45.6 bar, with a total mass flow rate of 100 kg/h. This feed is directed into a conversion reactor (CRV-100), where two reactions occur consecutively: the methanol synthesis reaction is presented in Equation (1) and the methanol dehydration reaction is presented in Equation (2) [9].

Both reactions are simulated using a conversion rate of 75% based on literature data (Figure 2). The reactor effluent exits at a temperature of 1,044 °C and a pressure of 45.6 bar, containing unreacted CO and H_2, residual methanol, water, and newly formed DME. At this condition, all components remain in the vapor phase. Due to the extremely high temperature of the reactor effluent, the stream undergoes a two-stage cooling process. The first cooling step is performed using Cooler 1 (E-100) with a duty of 100,000 kJ/h and a pressure drop of 20 kPa, reducing the temperature from 1,044 °C to 735.3 °C. At this temperature, the mixture remains entirely in the gas phase, thus requiring further cooling. The second cooling step uses Cooler 2 (E-101), which has a duty of 300,000 kJ/h and a pressure drop of 40 kPa, lowering the temperature to −96.88 °C. At this stage, most of the DME and methanol condense into the liquid phase, while syngas components (CO and H_2) remain in the gas phase. The resulting vapor fraction of 0.5801 indicates the presence of a two-phase mixture suitable for separation.

The cooled stream is then fed into a two-phase separator (V-100), where gas components exit from the top consisting mainly of unreacted H_2 and CO while the liquid phase containing DME, water, and residual methanol exits from the bottom for further purification. The initial unmodified simulation shows that from 100 kg/h of syngas, 39.65 kg/h of DME is produced, which is lower than the conversion achieved at laboratory scale. Therefore, process optimization was carried out using a case-study approach.

The first optimization involved varying the mole fraction of H_2 in the syngas feed between 0.5 and 0.8. The simulation results revealed that the optimal H_2 mole fraction is 0.5999, yielding a maximum DME production rate of 41.6677 kg/h. Below this value, insufficient hydrogen limits the methanol synthesis reaction, while above this threshold, additional H_2 no longer enhances DME production because the reaction conversion is already at its maximum. The second optimization focused on adjusting the cooling duty of Cooler 1. Increasing the cooling duty produced lower temperatures and enhanced DME condensation, thereby improving phase separation. However, Cooler 1 alone could only reduce the effluent temperature to 735.3 °C, necessitating the use of Cooler 2 to achieve the required condensation temperature for DME.

The overall production of dimethyl ether (DME) involves two reaction steps. The first step is the synthesis of methanol, which is formed through the catalytic hydrogenation of carbon monoxide or carbon dioxide. In the subsequent step, methanol undergoes a dehydration reaction to produce DME, with water generated as the only by-product. To determine whether these reactions are exothermic and to assess their reaction

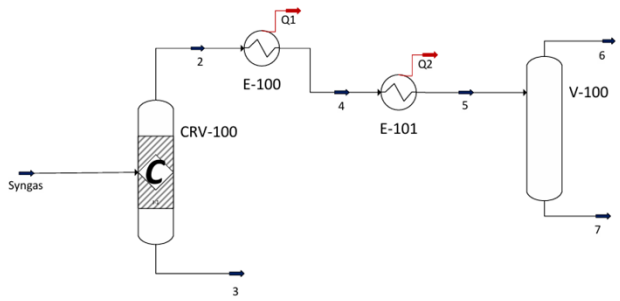

Figure 1. The basic (unmodified) process flow diagram of dimethyl ether.

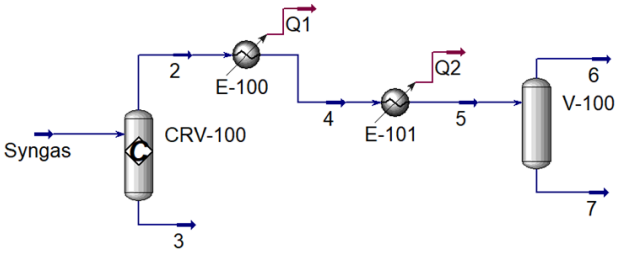

Figure 2. Aspen HYSYS process simulation for unmodified/before modification [15].

direction particularly whether they proceed irreversibly, it is necessary to calculate the standard heat of reaction ($\Delta H°_{298}$) at 1 bar and 298 K using the standard heats of formation of the reactants and products. The corresponding standard enthalpy of formation ($\Delta H_f°$) and Gibbs free energy of formation ($\Delta G_f°$) for all species involved are summarized in Table 1.

Standard heat of reaction at 298 K ($\Delta H°_{298\ K}$) for synthesis of methanol:

$(\Delta H°_{298K}) = \Sigma\ \Delta H_f°_{product} - \Sigma \Delta H_f°_{reactan}$
$= (\Delta H_f°\ CH_3OH) - (\Delta H_f°\ CO + \Delta H_f°\ H_2)$
= -91.0 kJ/mole
Standard heat of reaction at 298 K ($\Delta H°_{298\ K}$) for dehydrogenation process:

$(\Delta H°_{298K}) = \Sigma\ \Delta H_f°_{product} - \Sigma \Delta H_f°_{\ reactant}$
$= ((2\times\Delta H_f°\ CH_3OCH_3) + \Delta H°_f\ H_2O)) - (2\times\Delta H_f°\ CH_3OH)$ = -12.0 kJ/mole

Based on the calculations, the standard heats of reaction ($\Delta H°_{298}$) for the methanol synthesis and subsequent dehydration processes are −91.0 kJ/mol and −12.0 kJ/mol, respectively. The negative values indicate that both reactions are exothermic, releasing heat as they proceed.
Gibbs free energy change for synthesis of methanol:

$\Delta G°_{298K} = \sum_{\Delta G_f°} product - \sum_{\Delta G_f°} reactant$
$= \left(\Delta G_f°\ CH_3OH\right) - (\Delta G_f°\ CO + \Delta G_f°\ H_2)$
= -25.2 kJ/mole
$\Delta G°_{298K} = -R\ T \ln K_{298}$
$\ln K_{298} = \frac{\Delta G°_{298K}}{-R\ T}$
K_{298} = 26139.43
At operating reactor temperature of 225 °C (498.15 K):
$\ln \frac{K_T}{K_{298}} = -\frac{\Delta H°_{298K}}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right)$
$K_{498.15} = 1.1052\times10^2$
Gibbs free energy change for dehydrogenation process:
$\Delta G°_{298K}$ $= ((\Delta G_f°\ CH_3OCH_3) + \Delta G°_f\ H_2O) - (2 \times \Delta G_f°\ CH_3OH)$ = -16.91 kJ/mole
$\Delta G°_{298K} = -R\ T \ln K_{298}$

Table 1. The value of $\Delta H_f°$ and $G_f°$ of components [15].

Compound	Molecular Formula	$\Delta H_f°$ kJ/mole	$\Delta G_f°$ kJ/mole
Carbon monoxide	CO	-110.5	-137.2
Hydrogen	H_2	-241.8	-228.6
Water	H_2O	-201	-162.3
Methanol	CH_3OH	-184.1	-112.9
Dimethyl ether	CH_3OCH		

$\ln K_{298} = \frac{\Delta G°_{298K}}{-R\ T}$ = 6.8252
K_{298} = 920.76
At operating reactor temperature of 260 °C (533.15 K):
$\ln \frac{K_T}{K_{298}} = -\frac{\Delta H°_{298K}}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right)$
$K_{498.15}$ = 13.0724

Overall, the DME production process through methanol formation followed by methanol dehydration achieves optimal performance at an H_2 mole fraction of 0.5999, producing up to 41.67 kg/h of DME. The process requires two cooling units to ensure that DME reaches the liquid phase before entering the separator, and the selection of appropriate operating conditions significantly influences both reaction conversion and product separation efficiency.

3.2. Process Modification

To maximize the yield of DME, the production process was modified through the addition of a cooler, valve, heater, and distillation column, along with an increase in reactor conversion. The cooler was introduced because higher DME conversion led to a significant rise in outlet temperature, necessitating cooling to maintain optimal conditions for the stream entering the separator. The temperature must be controlled to remain within a range that allows effective separation to maintain the stability of DME and prevent degradation, while the operating pressure influences the boiling point and phase equilibrium in the distillation column. An increase in pressure tends to reduce the concentration of DME in the distillate product due to changes in vapor–liquid equilibrium; therefore, the pressure must be regulated to maximize the separation of DME from methanol and water [16]. As a result of these modifications, the DME yield increased to 97.6%. The modified process flow diagram for cyclohexane production is shown in Figure 3, and the corresponding Aspen HYSYS simulation is presented in Figure 4.

Dimethyl ether (DME) is produced from syngas at 225 °C and 4560 kPa, using CO and hydrogen as feedstock. The stream then enters the conversion reactor, where two reactions occur: methanol synthesis and subsequent methanol dehydration, achieving a conversion of 80%. Prior to separation, the reactor effluent is gradually cooled to −55.1 °C. Incorporating a separator enhances product yield by removing dissolved gases, thereby stabilizing the liquid phase of the mixture [16]. The separator functions to isolate unreacted syngas from the desired DME product. The residual syngas exits through the overhead stream as waste gas, while DME is recovered from the bottom stream as the primary product.

Dimethyl ether (DME) exiting the separator still contains methanol and water, necessitating further purification in a distillation column. Prior to entering the column, the mixture undergoes pretreatment through a valve and heater to adjust its pressure and temperature from −55.1 °C and 4500 kPa to 89 °C and 1040 kPa. This adjustment is essential because DME, methanol, and water possess different boiling points and form a complex azeotropic system. The presence of an azeotrope results in a constant boiling point, making conventional distillation challenging without modification of operating conditions [17]. Moreover, elevated pressure tends to lower the concentration of DME in the distillate due to shifts in vapor–liquid equilibrium; thus, pressure regulation is critical to optimize the separation of DME from methanol and water [18]. DME is obtained as the primary product, with methanol and water produced as a by-product. The simulation results for DME production are presented in Figure 4.

3.3. Improvement of Yield Product Due to the Process Modification

The modification process aimed at enhancing overall performance and conversion efficiency in dimethyl ether (DME) production was implemented through strategies emphasizing thermal control and optimization of the separation unit. In this study, a cooling unit was introduced to replace the previous temperature regulation method, ensuring stable operation even at high conversion levels. The inclusion of the cooler proved essential, as the methanol dehydration reaction exhibited a sharp temperature increase when conversion rose from 75% to 90%, resulting in an outlet temperature rise of approximately 100 °C. Without proper temperature management, excessive thermal conditions could shift the reaction equilibrium, alter phase behavior, and diminish separation efficiency [19]. To address this, the cooler maintains the stream temperature below the boiling point of DME, while remaining above the boiling points of syngas components. This balance allows DME condensation to occur optimally without premature condensation of CO and H_2 [20].

In the modified design, the incorporation of a cooler offers an additional advantage by gradually reducing the operational workload, as the target temperature of the stream entering the separator no longer requires extreme cooling. Whereas some studies on similar processes report that the separator inlet temperature must be lowered to around –95 °C, in this configuration cooling is only necessary to approximately –50 °C [21]. This more moderate temperature range enhances cooler efficiency, lowers energy consumption, and preserves the overall thermal stability of the process [22]. With more effective heat removal, reactor conditions can be maintained closer to the optimum, leading to an increase in conversion from 75% to 80%. This improvement simultaneously reduces the methanol recycle load and boosts energy efficiency without imposing additional thermal stress on the reactor.

The purification stage is enhanced through the incorporation of a valve and heater as a pre-treatment step prior to the stream entering the distillation column. This unit ensures that both pressure and temperature are properly conditioned for the three-component distillation process involving DME, methanol, and water. As a result, the distillation column can separate the mixture more effectively, supported by the thermal stability achieved through earlier control measures. The integration of the cooler, improved reactor conversion, and pre-treatment before distillation delivers superior and more consistent separation performance. Ultimately, the distillation column achieves a DME yield of up to 97.6%, representing a substantial improvement in product recovery efficiency while contributing to more sustainable energy utilization across the entire production process.

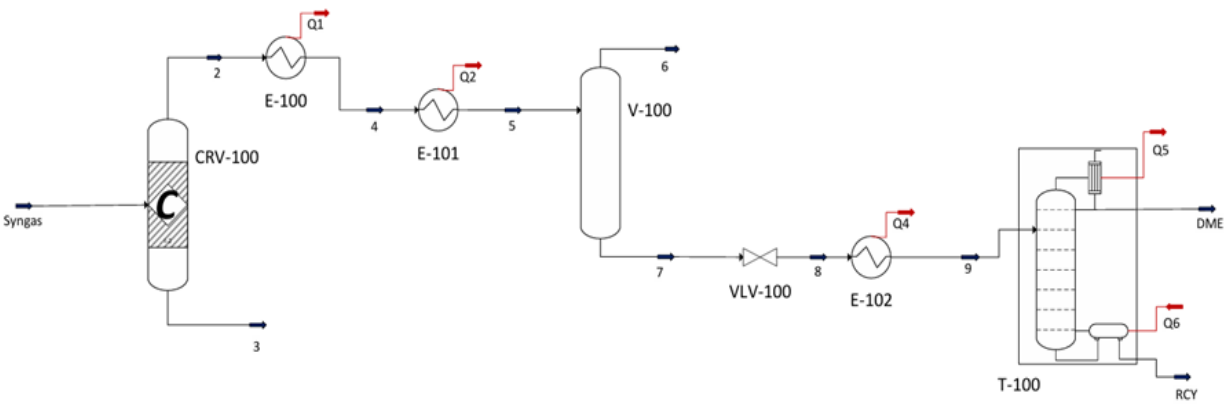

Figure 3. The modified process flow diagram of dimethyl ether.

4. Conclusions

The modification of the dimethyl ether (DME) production process has demonstrated significant enhancements in system performance, particularly in conversion efficiency, temperature regulation, and separation effectiveness. By incorporating a cooling unit and adjusting pressure and temperature conditions prior to distillation, the conversion rate increased from 75% to 80%, while the DME yield rose to 97.6%. Beyond ensuring thermal stability, these adjustments also reduced the demand for extreme cooling, thereby improving overall energy efficiency. Nonetheless, further investigation remains essential to fully assess energy consumption, evaluate the environmental implications of syngas utilization as a feedstock, and examine the behavior of azeotropic mixtures at industrial scale. Ultimately, these process modifications are expected to deliver not only technical optimization but also long-term sustainability in advancing the transition toward low-carbon energy.

CRedit Author Statement

Author Contributions: M. E. Pratama: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing, Review, Software and Editing, Supervision; G. T. A. Nugraha: Conceptualization, Methodology, Formal Analysis, Data Curation, Writing Draft Preparation, Visualization, Software, Project Administration; F. A. Maulana: Validation, Writing Draft, Review and Editing, Data Curation; M. H. Safrudin: Validation, Investigation, Resources, Writing Draft, Review and Editing, Validation; F. A. Afdika: Validation, Investigation, Resources, Data Curation, Writing Draft, Review and Editing. D. Amaanullah: Investigation, Resources, Data Curation, Review and Editing. All authors have read and agreed to the published version of the manuscript.

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