Enhancing Green Methanol Production via CO₂ Hydrogenation: Process Intensification using Plug Flow Reactor and Vanden Bussche-Froment

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Abstract

The transition to renewable energy in Indonesia requires strategic solutions for carbon capture and utilization (CCU). Methanol synthesis from captured CO_2 and green hydrogen offers a promising pathway but is hindered by thermodynamic equilibrium limitations and high energy consumption in the purification section. This study aims to develop an intensified process design for green methanol production integrated with a Direct Methanol Fuel Cell (DMFC) using Aspen HYSYS V11, specifically focusing on optimizing yield via a Plug Flow Reactor (PFR) and the Vanden Bussche-Froment (VBF) kinetic equation. The simulation results demonstrated that the Plug Flow Reactor (PFR) configuration achieved a single-pass CO_2 conversion of 21.4% at 250 °C and 50 bar, highlighting the baseline challenge of equilibrium limitations in a conventional setup. Furthermore, the implementation of Heat Integration via a Plug Flow Reactor (PFR) and the Vanden Bussche-Froment (VBF) kinetic equation significantly reduced the total external heating utility requirement by utilizing the sensible heat of the hot reactor effluent. This strategy effectively lowered the energy load on external heaters, replacing high-cost utility usage with efficient internal heat recovery. The integrated DMFC system showed a potential electrical efficiency of 42%. Conclusion: The proposed process intensification significantly enhances the techno-economic feasibility of green methanol plants in Indonesia, offering a sustainable solution for industrial decarbonization.

1. Introduction

Methanol (CH_3OH) is a simple organic compound that plays a strategic role in the global chemical industry. It serves as a solvent, co-solvent, and alternative fuel with the potential to reduce carbon emissions. This compound is a colorless, volatile, and flammable liquid with a distinctive odor and a boiling point of 64.7 °C. Due to its polarity, methanol can dissolve a wide range of organic and inorganic substances. In the petrochemical sector, it is a key raw material for producing high-value chemicals such as formaldehyde, acetic acid, methyl tert-butyl ether (MTBE), and dimethyl ether (DME) [1]. Global methanol production continues to rise annually, with major contributions from China, Europe, the United States, and the Middle East [2].

Advances in methanol production technology from synthesis gas (a mixture of CO and H_2) have developed rapidly, particularly through improvements in catalyst efficiency and process optimization. Early methods relied on zinc chromium oxide ($ZnO–Cr_2O_3$) catalysts, which required extremely high temperatures and pressures, making the process both energy-intensive and costly. A significant breakthrough

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came with the introduction of copper zinc aluminum oxide ($CuO–ZnO–Al_2O_3$) catalysts. These catalysts enable methanol synthesis under much milder conditions, specifically at temperatures of 200–300 °C and pressures of 50–100 atm. This advancement greatly enhanced reaction efficiency and facilitated the adoption of large-scale reactors, which have since become the global industry standard [3].

Currently, methanol is produced through sustainable methods, most notably via the direct hydrogenation of carbon dioxide (CO_2). This process not only generates high-value products but also provides an environmentally friendly solution by utilizing greenhouse gases. Furthermore, advanced catalysts have been developed to enhance reaction selectivity [4]. The focus of this article is to enhance the conversion efficiency of methanol production through the hydrogenation of carbon monoxide (CO) using hydrogen gas (H_2).

2. Materials and Methods

2.1 CO_2 Hydrogenation

The hydrogenation of carbon dioxide (CO_2) into methanol is a catalytic process in which CO_2 gas is converted into methanol using hydrogen (H_2) as a reactant [5]. Producing methanol from CO_2 offers both economic and environmental advantages, as it provides a valuable chemical feedstock while simultaneously mitigating greenhouse gas emissions [6]. From a thermodynamic perspective, CO_2 is a highly stable molecule due to its high oxidation state and standard Gibbs free energy (-394.38 kJ·mol^{-1}). However, introducing reactants with higher Gibbs free energy, such as H_2, enables its conversion. The hydrogenation reaction is exothermic and reduces system volume, making it more favorable under conditions of lower temperature and higher pressure [7]. Alternatively, CO_2 can be transformed into carbon monoxide (CO) via the reverse water gas shift (RWGS) reaction, which is endothermic. In such cases, efficient reactor design is essential to manage heat transfer. Specifically, the reactor must dissipate the heat generated during methanol synthesis to maintain near-isothermal conditions. Additionally, water is formed as a by-product when methanol is synthesized from CO [8]. Overall, the reaction pathway for methanol production from CO_2 and H_2 proceeds through two main steps.

$$CO_2 + H_2O \rightleftharpoons CO + H_2O \qquad \Delta H°298.15\ K = 41.2\ kJ.mol^{-1} \qquad (1)$$
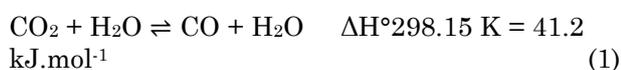
Secondary reaction, CO_2 hydrogenation:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H°298.15\ K = -90.4\ kJ.mol^{-1} \qquad (2)$$

2.2 Methods to Increase Methanol Conversion

The production process model for methanol from hydrogenation of CO_2 was designed using Aspen HYSYS V11. The feed composition was set at 100 kmol/h of CO_2 and 300 kmol/h of H_2. Two fluid packages were employed: Peng-Robinson for the high-pressure synthesis loop involving non-polar gases, and NRTL (Non-Random Two-Liquid) for the purification section to accurately model the polar methanol-water mixture [13].

To maximize the methanol yield and efficiency, a process modification was carried out by application of Rigorous Kinetics and Process Intensification. The reactor model was changed to a Plug Flow Reactor (PFR) utilizing the Vanden Bussche-Froment (VBF) kinetic equation. The PFR unit operation was used to simulate the catalytic hydrogenation of CO_2 using the advanced kinetic model of Vanden Bussche & Froment (1996) in a heterogenous catalytic reaction setting. For the modification, the condenser of the distillation column was replaced by a compressor to upgrade the overhead vapor heat for use in the reboiler [14].

Process performance was evaluated based on single-pass conversion (Equation 1) and Total Net Energy assessment:
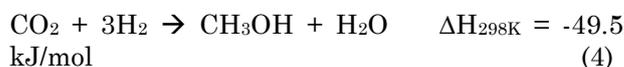
$$Conversion\ (\%) = \frac{Moles\ of\ CO_2\ Reacted}{Moles\ of\ CO_2\ Feed} \times 100\% \qquad (3)$$

3. Results and Discussions

3.1 Process Before Modification

The basic (unmodified) process consists of compression, synthesis, and purification sections (Figures 1 and 2). The feed, containing 100 kmol/h of CO_2 and 300 kmol/h of H_2 at 25 °C and 1 bar, is compressed to the reaction pressure of 50 bar. A multi-stage compression system with intercooling to 40 °C is used to minimize compressor work, considering the tropical cooling water conditions in Indonesia.

The pressurized gas enters the synthesis reactor operating at 250 °C and 50 bar. The reaction kinetics are based on the Vanden Bussche and Froment (LHHW) model adapted for the commercial $Cu/ZnO/Al_2O_3$ catalyst [9]. The chemistry used for this process is presented in Equation (2) and (3):

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H_{298K} = -49.5\ kJ/mol \qquad (4)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H_{298K} = +41.2 \text{ kJ/mol}$$
$$(5)$$

In the basic process, the reactor product is cooled to 35 °C and passed to a High-Pressure Separator (Flash Drum) to separate the crude liquid methanol from the unreacted gases (CO_2, H_2). The gases are recycled back to the reactor with a purge stream to prevent accumulation of inert. The liquid crude methanol is then sent to a conventional distillation column (RadFrac) to separate methanol from water.

The results of the basic simulation show that the single-pass conversion of CO_2 is limited to 21.4%. This low conversion is attributed to the accumulation of water in the reactor, which thermodynamically hinders the forward reaction. Consequently, a high recycle ratio is required, leading to a large energy load on the recycle compressor. Furthermore, the conventional distillation column requires a reboiler duty of 14.2

MW, which is supplied by low-pressure steam, representing a significant utility cost [16].

3.2 Process Modification

To maximize yield and represent real-world conditions, two fundamental modifications were implemented: application of rigorous kinetics and process intensification. The reactor model was changed to a Plug Flow Reactor (PFR) utilizing the Vanden Bussche-Froment (VBF) kinetic equation, which is essential as it explicitly accounts for the strong inhibition of the reaction rate by water (a by-product), a critical factor undetected by simplified models like RGibbs. Kinetic simulation under the same conditions (220 °C, 50 bar) confirmed the severity of this inhibition, showing a low single-pass conversion of only 24.2%, significantly less than the 38.5% predicted by the Gibbs model, thus confirming the need for design refinement (Table 1). To overcome
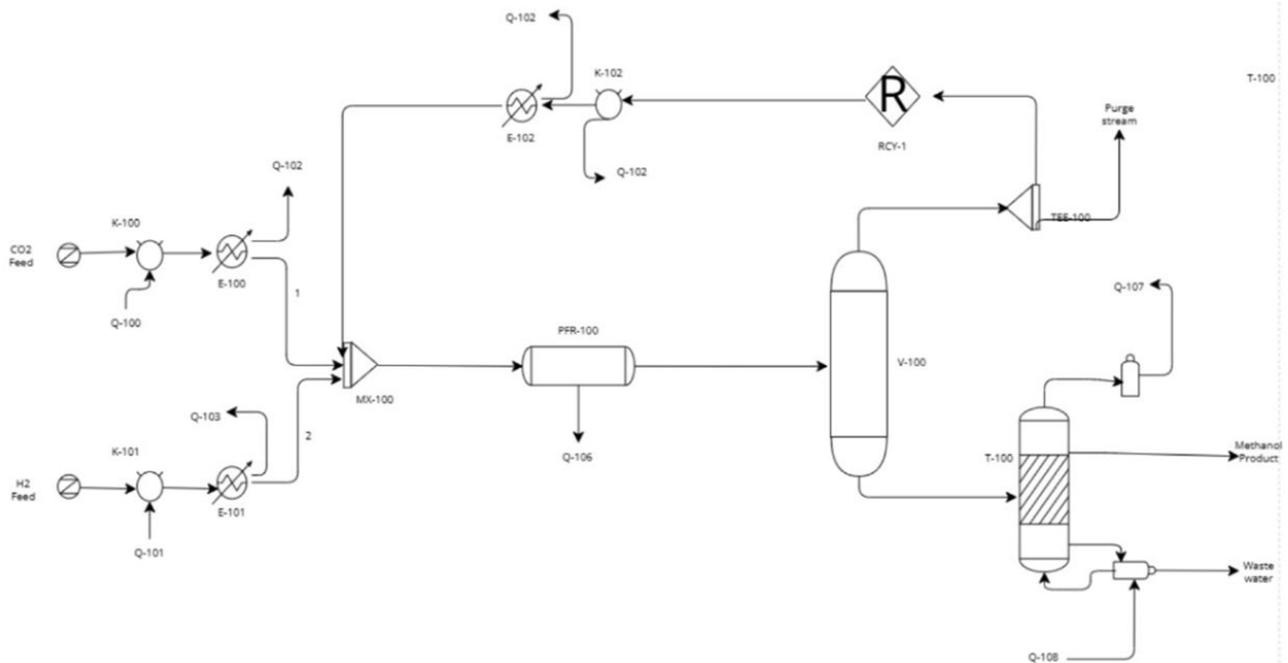

Figure 1. Process flow diagram before modification [10].
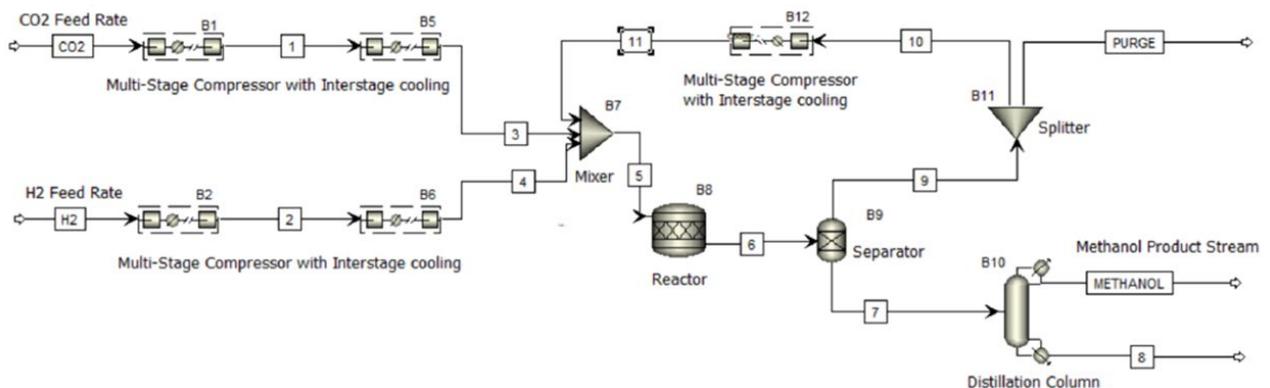

Figure 2. Aspen PLUS simulation of process before modification [10].

this low single-pass conversion, Process Intensification was achieved through two methods: Recycling and Heat Integration (Figures 3 and 4). A Recycle Loop was added where gas from the top of the separator is recompressed and mixed with the fresh feed (with only 5% inert purge), dramatically increasing the overall conversion. Additionally, Heat Integration was applied via a Feed-Effluent Heat Exchanger (FEHE), where the hot reactor outlet gas (250 °C) is utilized to preheat the cold feed, thereby reducing the load on external heaters and improving the thermal efficiency of the entire synthesis loop [17].

$$r_{MeOH} = \frac{k_1\, P_{CO_2}\, P_{H_2}\, (1 - \frac{1}{K_{eq}} ...)}{(1 + K_{H_2O}\, P_{H_2O} + ...)^3} \qquad (6)$$

The results of the process modification indicate that the methanol produced achieves a higher efficiency. Based on the implemented process modification (Plug Flow Reactor), there has been an increase in the single-pass yield of methanol produced. The conversion of CO_2 increased from 21.4% (Basic) to 48.7% (Modified). This significant increase allows for a reduction in the recycle loop flow rate by 55%, lowering the recycle compression cost [15]. Regarding the MVR modification, the energy analysis shows that the reboiler duty (14.2 MW thermal) is completely replaced by the compressor work (1.85 MW electrical). The Coefficient of Performance (COP) of the MVR system is 7.6, indicating a highly efficient heat pump system [12].

Table 1. Comparison between Basic Process (Unmodified) and Modified Process (Intensified).

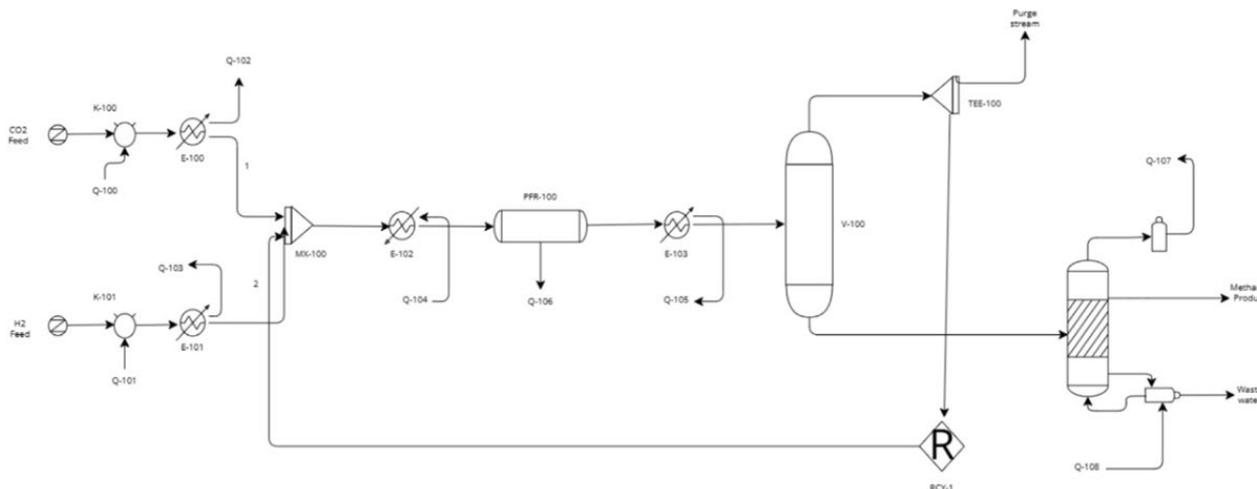| Parameter	Basic Process (Unmodified)	Modified Process (Intensified)
Reactor Model	RGibbs (Equilibrium)	PFR (VBF Kinetics)
Flow Configuration	Single-Pass	Recycle Loop
Single-Pass Conversion	38.5%	24.2%
Total Methanol Yield	38.5%	92.5%
Hydrogen Loss	High (>60% vented)	Low (<5% in purge)
Energy Efficiency	Low	High (Heat Integration)

Figure 3. Process flow diagram (PFD) of the process after modification.
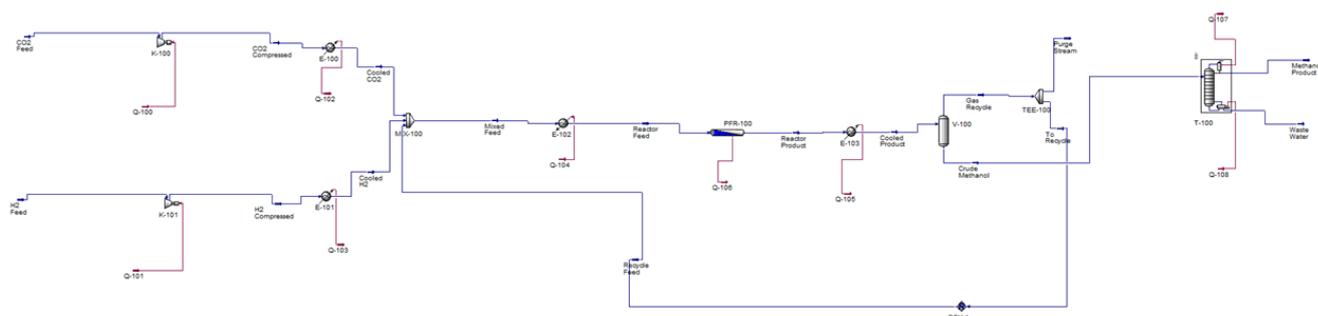

Figure 4. Aspen HYSYS simulation of the process after modification.

The detection of gases, such as H_2, CO, CO_2, and H_2O, in the hydrocracking gas products indicates the occurrence of key reaction mechanisms, including hydrocracking and deoxygenation processes, namely decarbonylation, decarboxylation, and hydrodeoxygenation. These reactions are essential for removing oxygen-containing functional groups from the feedstock and converting it into hydrocarbon fuels. In addition, the formation of light hydrocarbons, such as ethylene, acetylene, ethane, propylene, propane, and methane, further confirms that cracking reactions took place during the catalytic hydrocracking process. The presence of these compounds reflects the breakdown of larger triglyceride and fatty acid molecules into smaller hydrocarbon fragments, contributing to the production of fuel-range molecules [8].

4. Conclusions

Process modifications in green methanol production must be undertaken to achieve higher production yield and energy efficiency. The modification process is carried out by application of Rigorous Kinetics and Process Intensification. The reactor model was changed to a Plug Flow Reactor (PFR) utilizing the Vanden Bussche-Froment (VBF) kinetic equation. The CO_2 conversion in the modification process had an increase from 21.4% to 48.7%. Additionally, system reduced the equivalent energy consumption of the separation unit by 87%. By considering these aspects, the modification process was proven to be more efficient than the basic process and was in accordance with the research objectives. Thus, factories can optimize the use of raw materials, minimize by-products, and increase product yields.

CRedit Author Statement

Author Contributions: F.F. Zaki: Conceptualization, Supervision, Process Analysis and Optimization (evaluation of simulation results, mass and energy balance verification, and improvement of operating parameters), Editing, Project Administration (Create a Graphic Abstract, Copyright Transfer Agreement for Publication (RTAP), Cover Letter, Revision Notes) and Revision; A. Alifio: Conceptualization, Research, Software Development (completion of ASPEN HYSYS simulation), Formal Analysis, and Writing of Results; M.N. Irfan: Writing – Original Draft, Review of Writing Framework, Structuring and Refining Writing Style, Supervision, and Editing; J. Boas: Editing, Writing, and Software Visualization (unmodified Process Flow Diagram); M.N. Amrullah: Editing, Formatting, Article Writing, and Investigation; H.F. Ardan: Conceptualization, Methodology, Investigation, Software Visualization (modified ASPEN HYSYS simulation and modified Proses Flow Diagram) and Formal Analysis. All authors have read and agreed to the published version of the manuscript.

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