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Assessing the economic viability of green methanol production: The critical role of CO_2 purity in green methanol production

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ABSTRACT

The growing concern over climate change and rising carbon dioxide (CO_2) emissions have spurred the development of strategies to upcycle greenhouse gases. One promising solution is the synthesis of green methanol via catalytic hydrogenation of captured CO_2 using renewable hydrogen (H_2). This provides a versatile chemical feedstock for fuels and industrial processes while reducing CO_2 levels. Recent advancements in CO_2 capture technologies achieve purities ranging from 83% to 98% (v/v), enabling a sustainable integration with green hydrogen for methanol production. While research has largely focused on CO_2 purities above 96%, such models overlook the variability and lower purities typical of industrial carbon capture streams. Addressing this gap, this study examines the economic impacts of CO_2 purity on methanol synthesis. Using Aspen Hysys V14, the hydrogenation process is simulated to assess the effects of varying CO_2 purities on operational costs, yield, and profitability, providing a realistic evaluation under actual industrial conditions. The results reveal that even slight changes in CO_2 purity markedly influence both costs and profitability, highlighting the importance of studying CO_2 capture technologies for methanol production. This study quantifies the relationship between CO_2 purity and operational cost, contributing critical insights for process operation. By emphasizing the role of CO_2 purity in enhancing both sustainability and economic feasibility, it advances the understanding of green methanol production as a viable strategy for climate change mitigation.

Keywords: CO_2 hydrogenation, Green methanol production, Techno-Economic Analysis.

INTRODUCTION

Anthropogenic emissions of carbon dioxide (CO_2) have surged dramatically in the past century, becoming a central focus of climate change mitigation efforts. The overwhelming scientific consensus indicates that the increase in atmospheric CO_2 concentration is strongly correlated with the rise in global temperatures, prompting the development of technologies to capture and utilize CO_2 [1]. Among these, the conversion of CO_2 into value-added products has garnered significant attention as a strategy to mitigate emissions while supporting the transition to a circular carbon economy.

Approximately 35% of global anthropogenic CO_2 emissions stem from industrial processes and power generation reliant on fossil fuels [2]. While capturing CO_2 from these sources is technically feasible, the associated costs remain high due to the energy-intensive nature of capture and compression processes [3]. Integrating CO_2 utilization into this framework offers an opportunity to offset costs by transforming CO_2 into marketable products, such as methanol, thereby enhancing the economic viability of carbon capture initiatives.

Methanol is a key platform chemical widely used in the production of formaldehyde, acetic acid, and methyl tert-butyl ether. It is also an alternative fuel with excellent combustion properties, presenting fewer environmental pollutants compared to conventional fossil fuels [4].

The quality of the CO2 feedstock is crucial for the upcycling process. Research has largely focused on CO_2

purities above 96% (v/v) [5]. However, recent advancements in CO_2 capture technologies achieve purities ranging from 83% to 98% (v/v) [6]. Hence, this study aims to evaluate the impact of CO_2 purity on the production of fuel-grade methanol, considering the technical and economic implications of integrating CO_2 capture and utilization processes efficiently. By focusing on the catalytic hydrogenation of CO_2 under varying purity levels, the research quantifies the potential for emission abatement and economic feasibility, thus contributing to the broader adoption of sustainable methanol synthesis technologies.

Methanol production process

Traditionally, methanol is synthesized from synthesis gas—a mixture of carbon monoxide (CO), CO_2, and H_2—derived predominantly from natural gas via steam methane reforming [7]. The increasing emphasis on sustainability has driven interest in alternative feedstocks and processes for methanol production. Among these, the production of methanol from captured CO_2 through catalytic hydrogenation using renewable hydrogen (H_2) represents a genuinely green alternative, offering a pathway to reduce dependency on fossil fuels while enabling the recycling of CO_2 into valuable chemicals.

The direct hydrogenation of CO_2 to methanol in a single reaction step is simpler and more efficient [8] This method eliminates the need for intermediate processes, such as syngas production, required by traditional methods. Streamlining the reaction pathway not only reduces energy consumption but also lowers process complexity, improving overall economic feasibility and making it more suitable for large-scale applications. Additionally, it avoids the complex handling of CO and CO_2, which further enhances its compatibility with carbon capture and storage technologies [9].

This process not only facilitates CO_2 recycling but also contributes to the substitution of fossil feedstocks in methanol production, reducing the overall carbon footprint of the chemical industry. This process typically employs $Cu/ZnO/Al_2O_3$ catalysts, which operate under moderate conditions (210–270°C, 50–100 bar) with high selectivity (<99%) for methanol [10].

Yet, the economic and environmental impact of this process is highly dependent on the purity of the captured CO_2 and the energy used for hydrogen production.

CO_2 hydrogenation

Methanol can be synthesized from CO_2 through two main pathways: a one-step process or a two-step process. The one-step pathway involves the direct hydrogenation of CO_2 to methanol, while the two-step process first converts CO_2 to CO via the Reverse Water Gas Shift (RWGS) reaction, followed by hydrogenation of CO to methanol. In this study, the one-step hydrogenation of CO_2 was selected as the conversion method.

The CO_2 utilized in these processes can be sourced from flue gases emitted by thermal power plants (e.g., coal or natural gas-based), as well as from industrial facilities such as steel mills, cement plants, and other significant CO_2 emitters.

The hydrogen required for this reaction must be produced sustainably, for instance, via biological methods using algae or through water electrolysis powered by carbon-neutral electricity sources [11].

The production of methanol is achieved through highly exothermic reactions (Eqs. 1, 2), while the RWGS reaction (Eq. 3) may also proceed in parallel. These reactions collectively enable the valorization of CO_2 into a versatile chemical with broad industrial applications.

$$\mathrm{CO_{(g)} + 2H_{2\,(g)} \leftrightarrow CH_3OH_{(l)}} \quad \Delta H_{298K} = -128\ \frac{\mathrm{kJ}}{\mathrm{mol}} \tag{1}$$

$$\mathrm{CO_{2\,(g)} + 3H_{2\,(g)} \leftrightarrow CH_3OH_{(l)} + H_2O_{(l)}} \quad \Delta H_{298K} = -87\ \frac{\mathrm{kJ}}{\mathrm{mol}} \tag{2}$$

$$\mathrm{CO_{2\,(g)} + H_{2\,(g)} \leftrightarrow CO_{(g)} + H_2O_{\,(l)}} \quad \Delta H_{298K} = 41\ \frac{\mathrm{kJ}}{\mathrm{mol}} \tag{3}$$

The hydrogenation of CO_2 to produce methanol has garnered significant attention in recent years. Joo et al. investigated a two-step methanol production process and observed higher yields compared to the one-step alternative [12]. Mignard et al. proposed a process that synthesizes methanol from CO_2 captured from coal-fired power plant flue gases, using electrolytic hydrogen. Their findings highlighted that the availability of waste heat from the power plant is crucial to supply the thermal energy needed for substantial CO_2 abatement [13]. Without this thermal integration, CO_2 mitigation is negligible.

Methanol production emerged as the most energy-efficient route. Pontzen et al. compared the performance of CO_2-based methanol production over a $Cu/ZnO/Al_2O_3$ catalyst with conventional synthesis gas processes, finding that the CO_2-based process exhibited lower productivity levels [14].

Soltanieh et al. conducted an economic analysis for co-producing methanol and electricity from captured CO_2 and carbon-free hydrogen, emphasizing the potential for integrated systems [15]. Van Der Ham et al. proposed a CO_2-to-methanol process utilizing a fluidized-bed membrane reactor, which achieved significant CO_2 reduction [16]. However, the process faced challenges related to economic feasibility.

These studies collectively underscore both the technical promise and the economic hurdles associated with methanol production from CO_2 hydrogenation.

METHODOLOGY

Operational analysis and simulation were carried out using Aspen HYSYS V14 with stoichiometric feed conditions tailored to the methanol synthesis reaction. Thermodynamic properties of high-pressure streams (>10 bar) were modeled using the Redlich-Kwong-Soave equation of state, while the NRTL model was employed for streams at lower pressures (<10 bar). These thermodynamic models ensure robust and reliable process representation, optimizing performance across varying conditions. Sensitivity analysis of CO_2 purity were carried out for a given operational case study in methanol hydrogenation, evaluating its impact on process performance and efficiency. The simulated data obtained were used for the subsequent economic analysis. Hence, a relationship between feed purity and overall process economics was set by correlating these data with operating costs.

Case study

The process utilizes CO_2 sourced from any industrial facility emitting significant amounts of CO_2, coupled with hydrogen produced via water electrolysis, as feedstock for methanol synthesis. A schematic representation of the process is shown in **Figure 1**.

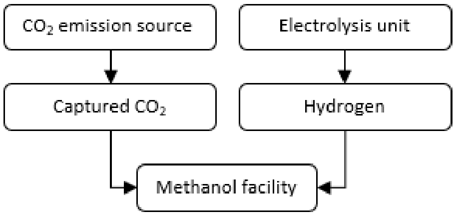

Figure 1. Scheme of methanol synthesis.

Water electrolysis is powered by carbon-free electricity sources such as renewables (e.g., hydroelectric, wind, solar, or biomass) or nuclear power. The entire system, including both hydrogen production and methanol synthesis, is designed to operate as an integrated unit, minimizing energy losses and simplifying logistics. This integration ensures that the hydrogen generated is directly utilized within the methanol synthesis process, avoiding storage and transportation challenges.

Water electrolysis unit

The production of hydrogen via water electrolysis (Eq. 4) requires an energy input of 60 kWh/kg H_2 [17]. The hydrogen exits the electrolyzer at 6 bar and 25 °C, ready for direct use in the methanol synthesis process.

$$H_2O_{(l)} \rightarrow H_{2\,(g)} + 0.5\,O_{2\,(g)} \tag{4}$$

Electrolysis also produces a significant quantity of oxygen as a by-product. This oxygen could be internally used in the power plant for oxycombustion, enhancing CO_2 concentration in flue gases and lowering the energy requirements for its capture. Alternatively, it can be marketed. This study analyses the first option.

CO_2 capture unit

The CO_2 capture unit considered in this paper relies on physical adsorption using adsorbents materials. In this process, CO_2 is captured from flue gases of industrial sources through its interaction with the adsorbent.

Flue gases containing CO_2 are first compressed to offset the pressure drop in the adsorption system. These gases are then introduced into the adsorbent bed, where the CO_2 is physically adsorbed due to the adsorbent's microporous structure. The system operates by cycling the pressure, with CO_2 being adsorbed at higher pressures. Once the zeolite becomes saturated with CO_2, the desorption process is initiated. This is achieved by reducing the pressure or increasing the temperature, which allows CO_2 to be released and collected for further utilization.

The adsorbent material can be regenerated after each cycle by applying pressure or temperature swing adsorption (PSA/TSA) methods [18], allowing it to be reused multiple times without significant loss of efficiency. The desorbed CO_2 is then captured and fed to the methanol synthesis unit, where it is combined with hydrogen.

The overall performance of the system depends on the adsorption capacity of the adsorbent, the frequency of regeneration cycles, and the efficiency of the desorption process [19].

CO_2 capture performance and associated energy use are influenced by the purity of the incoming CO_2 stream. Typically, the purity of captured CO_2 in industrial applications ranges from 83% to 98%. For CO_2 with a purity of 83%, the energy consumption for CO_2 capture can range between 1.00 kWh and 1.20 kWh/kg CO_2 [20]. When the CO_2 purity increases to 98%, the energy consumption for the same processes increases, typically between 1.50 kWh and 2.00 kWh/kg CO_2 [6], due to the need for higher efficiency in separating and adsorbing the CO_2 at greater purity levels. Estimations from industrial practice are shown in **Figure 2**. CO_2 is fed to the methanol plant at 6 bar and 25°C.

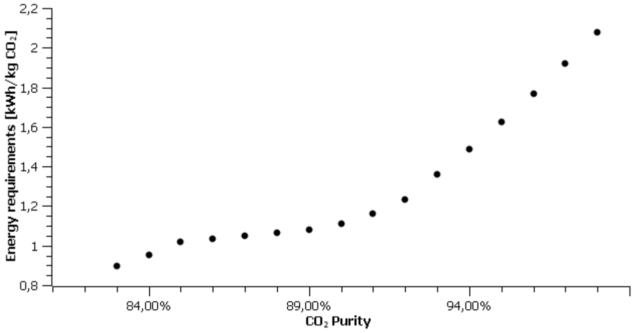

Figure 2. Energy demand for CO_2 purification.

Methanol synthesis and purification unit

The process flowsheet is presented in **Figure 3**. To analyze the operating modes of methanol production via CO_2 hydrogenation, a process flowsheet was developed for the methanol synthesis and purification stages. The conversion process utilizes a conversion reactor for CO_2

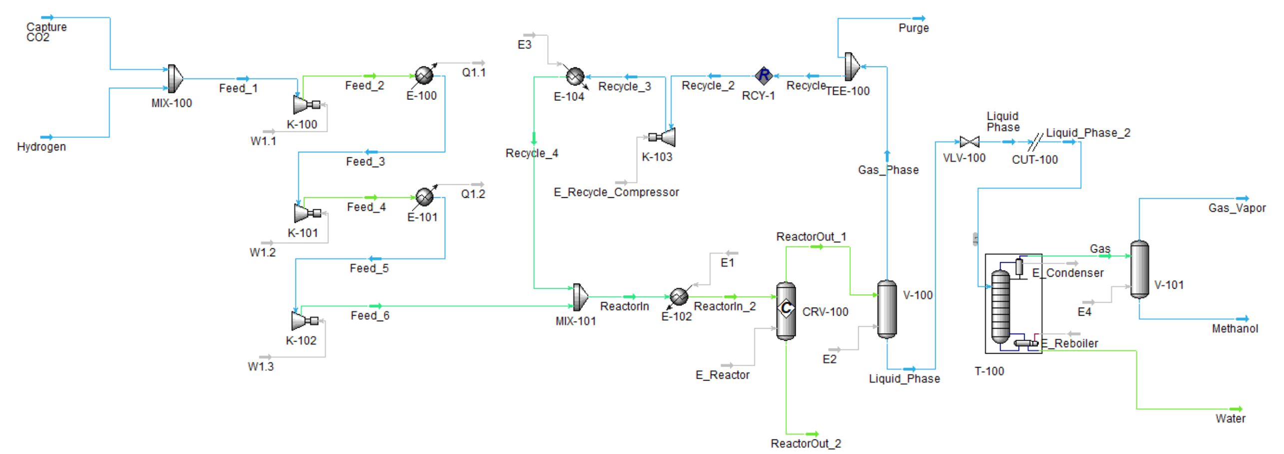

Figure 3. Flowsheet of the process for green methanol production from captured CO_2 and renewable hydrogen.

hydrogenation. Conversion reactor used for production of methanol works with 17.25 % of CO_2 conversion and the pressure is 60 bar [21].

The economic analysis assumes a base price of 50€/MWh for the energy cost [22]. Production cost is measured in kWh per kilogram of feed, reflecting the efficiency of the process and the energy requirements for transforming raw materials into the final product.

Process description

CO_2 and hydrogen is fed into the system at 6 bar, both at an initial temperature of 25 °C. The feed undergoes compression to the reaction pressure of 60 bar through a series of compressors with intercooling. The two compressed gases are initially mixed in MIX-100 and subsequently combined with the recycle stream.

The mixed stream is heated in E-102 to the desired reaction temperature (215ºC) before being introduced into the conversion reactor system. In these reactors, methanol synthesis occurs via the catalytic hydrogenation of CO_2. Heat generated during the reaction is managed through the reactor heat exchanger (E-Reactor).

The reactor outlet stream is sent to a flash separation unit (V-100), where it is divided into two phases. The gas phase, composed of non-reacted gases and by-products, is split into two streams: a small fraction is purged (5%) to prevent the accumulation of inerts and by-products, while the majority is compressed (K-103) and recycled back into the process, ensuring efficient use of unreacted reactants.

The liquid phase, containing methanol and water, is sent to the distillation column (T-100) for further purification. The crude methanol mixture undergoes pressure reduction via a valve system (VLV-100). The water by-product exits from the bottom of the column, while purified methanol vapor exits the top, where it is cooled and condensed to liquid form for collection.

RESULTS & DISCUSSION

The influence of CO_2 purity on the methanol synthesis process was analyzed, focusing on energy requirements (kWh/kg methanol), productivity (kg/h), recycle ratio, and production cost (€/kg methanol). Results are shown in **Figure 4**.

The recycle ratio decreases as CO_2 purity increases. At lower purities, higher amounts of inerts are recycled for the methanol synthesis, leading to increased operational demands on the system. Conversely, higher purities reduce recycle ratio, minimizing the energy for recycling equipment and improving overall system efficiency.

Methanol productivity increases proportionally with CO_2 purity. From an economic perspective, this increase in productivity directly offsets operational costs, making higher-purity CO_2 streams more favorable despite the potential increase in capture costs.

Lower purities result in greater energy demand due to the recycling of inert gases and increased compression requirements. As purity rises, energy consumption decreases significantly. This energy efficiency translates directly into reduced operational costs, particularly for systems where energy-intensive recycling and compression are dominant expenses.

The results highlight a non-linear relationship between CO_2 purity and methanol production costs. At lower purities, the cost remains relatively stable, suggesting that impurities within this range do not significantly impact the overall process economics.

As purity increases towards 89%, production costs rise and then fall for higher purities (>92%). This trend can be attributed to the balance between purification expenses and process efficiency. Intermediate purities like-

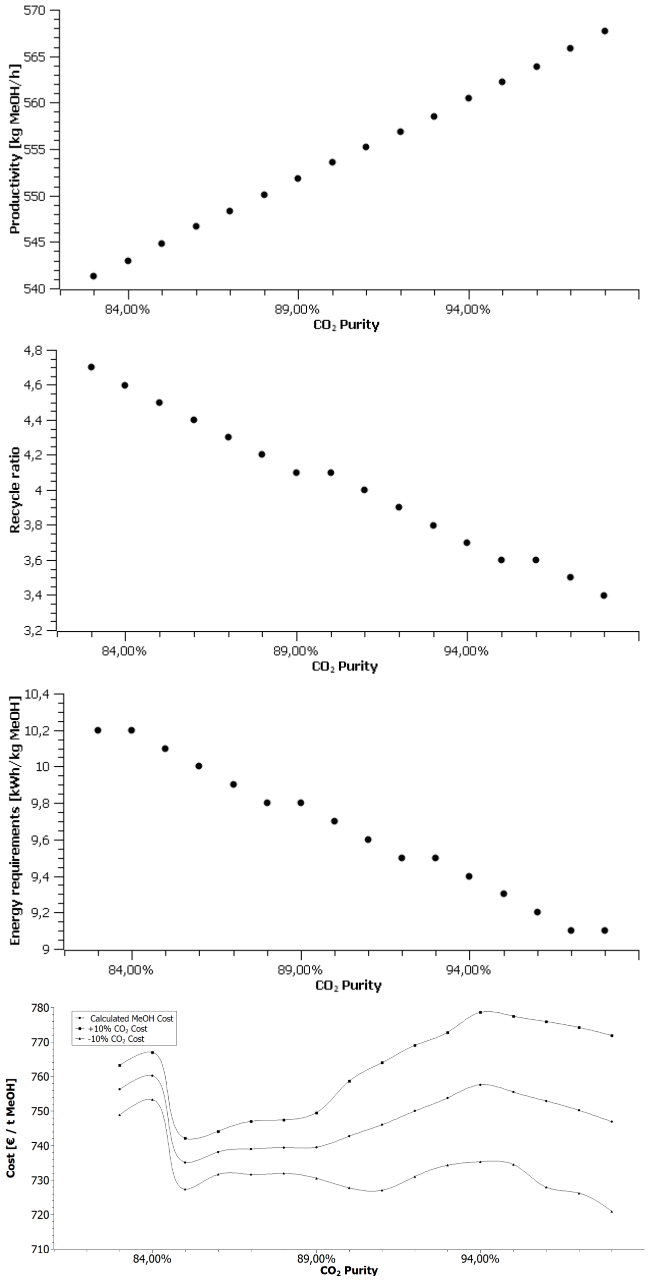

Figure 4. Effect of CO_2 purity on 1) Methanol productivity 2) Recycle ratio 3) Energy requirements 4) Cost of methanol production.

ly require additional separation steps, increasing operational costs. In contrast, at higher purities, methanol productivity increases while the energy requirements per unit of methanol decrease, leading to a reduction in overall production costs. As CO_2 purity increases toward 89%, production costs rise and can reach 770–780 €/t MeOH, indicating a local maximum. The ±10% cost lines bracket this baseline scenario, revealing how incremental shifts in CO_2 capture expenses can shift the overall cost curve by approximately 10–15 €/t.

CO_2 purity emerges as a decisive factor influencing operational costs. Lower purities introduce inefficiencies across multiple aspects of the process. Higher purities not only enhance productivity but also reduce operational costs, particularly in energy-intensive systems. The trade-off lies in balancing the cost of achieving higher CO_2 purity against the operational savings realized during methanol synthesis.

CONCLUSION

This study highlights the critical impact of CO_2 purity on green methanol production through catalytic hydrogenation, addressing a key gap in existing research focused primarily on high-purity CO_2 streams (>96%). Results demonstrates that higher CO_2 purity leads to reduced energy consumption, streamlined operational dynamics, and lower production costs, enabling optimal process performance. In contrast, lower CO_2 purities increase inert loads, energy demand, and recycle ratios, while excessively high purities elevate upstream costs, resulting in diminishing economic returns despite improved yields. These findings highlight the critical role of energy-efficient CO_2 capture technologies in enhancing the sustainability and economic viability of methanol synthesis. Moreover, it provides a foundation for further investigation into system optimization, supporting the development of green methanol production as a viable strategy for climate change mitigation.

This work contributes to the broader discourse on climate change mitigation by offering actionable insights into the interplay between CO_2 capture, purification, and utilization technologies.

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