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Biomethanol Production from Renewable Sources and CO_2 Derived from Biogas

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Methanol is a key chemical and fuel component, with increasing interest in renewable methanol production to reduce reliance on fossil fuels and mitigate carbon emissions. This study presents a sustainable process for methanol production from biogas, integrating biogas upgrading, methane steam reforming and CO_2 hydrogenation. A physical separation process using cold methanol at high pressure is implemented before the reforming and hydrogenation stages to selectively capture and purify CO_2 from biogas. The methane-rich stream undergoes reforming to produce syngas, supplying the hydrogen required for CO_2 hydrogenation and enhancing process efficiency. The overall process is modeled in Aspen Plus V12.1 to analyze system configurations and process parameters. The research framework evaluates the potential of biogas-derived methanol as a scalable and sustainable fuel alternative, supporting the transition to carbon-neutral chemical production. Additionally, a sensitivity analysis was conducted for both methane reforming and catalytic methanol synthesis reactions, aiming to identify optimal parameters for maximizing methanol production. This study investigates the efficiency and environmental impact of a biogas-based methanol production process, emphasizing CO_2 utilization and overall process performance. The CO_2 conversion efficiency reaches 99.22 %, with an overall process CO_2 conversion of 53.29 %. The process achieves net direct CO_2 emissions of -260.52 kmol/h, meaning it actively removes CO_2 from the atmosphere, and its carbon intensity is only 255.52 g CO_2 per kilogram of methanol- representing an overall direct emission reduction of up to 85 %.

1. Introduction

Burning fossil fuels, such as coal, oil, and gas, has emitted large amounts of CO_2, the main greenhouse gas responsible for global warming. It underscores the critical need to drastically reduce greenhouse gas emissions to address the already tangible impacts on the environment, biodiversity, and human societies (Luo et al., 2024). The potential of biogas as a renewable feedstock lies in its ability to serve as a sustainable and abundant source for producing chemicals like methanol, which are traditionally derived from fossil fuels. Biogas, primarily composed of methane and carbon dioxide, can be generated from organic wastes such as agricultural residues, food waste, livestock, and manure. This approach not only mitigates methane emissions—one of the most potent greenhouse gases, but also provides a dual benefit by utilizing CO_2, which is often considered a waste by product (Bube et al., 2024).

This research highlights that leveraging biogas for methanol production can significantly reduce greenhouse gas emissions compared to conventional methods relying on natural gas or coal. For example, studies emphasize that biogas-derived methanol could potentially lead to a carbon-neutral or even carbon-negative process, especially when coupled with renewable hydrogen production. Additionally, scaling up biogas utilization for methanol could contribute to global energy transitions by diversifying feedstock sources, reducing dependency on fossil fuels, and supporting circular economy principles (IEA Bioenergy, 2024).

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2. Biogas to syngas

2.1 Sources and compositions of biogas

Biogas, a gas fuel mixture mostly composed of methane (CH_4, 40–65 % vol/vol) and carbon dioxide (CO_2, 35–55 % vol/vol) with a lower concentration of hydrogen sulfide (H_2S, 0.1–3.0 % vol/vol), water (H_2O), and other trace compounds has an usual lower heating value in the range of 20 and 25 MJ/m^3 for CH_4 contents between 60 and 65 % (Zhao et al., 2020). Biogas production has the particularity that suits a variety of biological sources that are available in the form of unwanted materials; thus, it is considered as an accessible and decentralized energy carrier, which has had growing participation in the global energy matrix, representing nowadays 35 % of the energy produced from biomass sources (Mignogna et al., 2023).

Biogas composition differs based on the feedstock used, but CH_4 and CO_2 are the main components. The large variance of the CH_4, CO_2, H_2O, and O_2 content in biogas from different sources is a major challenge for biogas reforming. The biogas composition can be influenced by the feed composition, temperature, and organic loading rate (Jameel et al., 2024).

2.2 Hydrogen production from biogas

Hydrogen production from biogas typically involves the reforming of methane (CH_4) to produce syngas, which is then used for methanol synthesis or other applications. In this process, two key reactions are considered: the Methane Steam Reforming (MSR) and the Water-Gas Shift (WGS) reactions (Eq(1) and Eq(3)). MSR involves the conversion of methane and steam into carbon monoxide (CO) and hydrogen (H_2). However, additional side reactions, such as the reverse water-gas shift (RWGS) reaction (Eq(2)), can occur under certain conditions, where CO_2 reacts with hydrogen to produce CO and water. These side reactions can affect the hydrogen yield and overall efficiency of the process. Controlling the temperature, pressure, and catalyst properties can help mitigate these effects and optimize hydrogen production from biogas. The Water-Gas Shift (WGS) reaction plays a crucial role in hydrogen production from biogas. In this process, carbon monoxide (CO), which is produced during methane reforming, reacts with steam (H_2O) to form carbon dioxide (CO_2) and additional hydrogen (H_2) which help to achieve the desired hydrogen-to-carbon ratio for downstream applications, such as methanol synthesis. Optimizing reaction conditions and catalyst performance is critical to maximizing hydrogen production efficiency (Zhao et al., 2020).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^\circ = 206 \text{ kJ/mol} \tag{1}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^\circ = 41.2 \text{ kJ/mol} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^\circ = -41.2 \text{ kJ/mol} \tag{3}$$

Catalysts for reforming required to be thermally stable and coke resistant due to the endothermic nature of key reactions. Conventional supported nickel catalysts tend to deactivate due to coke formation and metal sintering. The most widely known catalysts for steam methane reforming is nickel catalyst supported by a wide range of materials including CeO_2, ZrO_2, and Al_2O_3 (Kumar and Kumar, 2024).

3. Methanol production

Methanol is recognized as a sustainable fuel alternative and important feedstock for various value-added chemicals. It plays an important role in chemical energy storage, enabling the conversion, transportation and long-term storage of renewable energy in a stable liquid form. Methanol is traditionally made from syngas, a combination of CO and H_2, which is primarily produced through the steam reforming of natural gas, according to CO Hydrogenation reaction (Eq(4)). In parallel to this reaction, over the commercially used $Cu/ZnO/Al_2O_3$ catalyst, CO_2 hydrogenation and the reverse water gas shift reaction (RWGS) occur (Eq(5) and Eq(2)), which allows converting the CO_2 produced during methane steam reforming:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H^\circ = -91 \text{ kJ/mol} \tag{4}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H^\circ = -49.1 \text{ kJ/mol} \tag{5}$$

However, conventional methanol synthesis is highly dependent on fossil fuels with high carbon intensity. Shifting to renewable pathways (biogas and CO_2 valorization) are necessary to align with climate goals and reduce greenhouse gas emissions.

Current study utilized methanol as a physical solvent for CO_2 separation from biogas, produced hydrogen from bi-reforming of methane, and finally generated methanol through CO_2 hydrogenation.

4. Carbon dioxide capture

Capturing CO_2 can be achieved via chemical (Molina and Bouallou, 2013) or physical absorption, depending on the process conditions. Oxy-combustion is another technology considered for CO_2 capture. It involves injecting pure oxygen (rather than air) during combustion. This prevents nitrogen (N_2) from entering the combustion chamber and being present in the flue gases. Washing and dehydration steps are sufficient to separate the CO_2 (Hagi et al., 2014). Chemical capture of CO_2 relies on solvents that chemically absorb and release CO_2 through reversible reactions (El Helou et al., 2025). Physical absorption of CO_2 relies on solvents that dissolve CO_2 without chemical reactions, making it suitable for high-pressure applications (Monzer and Bouallou, 2022). Methanol is widely recognized as an effective physical solvent for CO_2 absorption due to its high solubility for CO_2 at low temperatures and high pressures. The absorption process follows Henry's Law, where CO_2 dissolves into methanol without chemical reactions, making it particularly suitable for pre-combustion CO_2 capture and syngas treatment. One of methanol's key advantages is its high CO_2 loading capacity, especially when operated at cryogenic temperatures (as low as -100 °C). The low temperature increases CO_2 solubility and reduces methanol losses due to evaporation (Ban et al., 2014). Additionally, methanol shows low regeneration energy requirements, as CO_2 can be easily stripped by pressure reduction or mild heating without requiring chemical regeneration, unlike amine-based solvents. In this study, methanol is used as a physical solvent for CO_2 absorption, leveraging its high solubility to enhance gas separation efficiency (Soo et al., 2024).

5. Methods

5.1 Process simulation

In this work, biogas is assumed to be composed of CO_2 and CH_4 in a molar ratio of 0.65 (about 60 mol % of CH_4 and 40 mol % of CO_2). Process simulations have been performed using Aspen Plus V.12.1 and Peng-Robinson was selected as the EOS for predicting thermodynamic model for estimation of fluid proprieties. The CO_2 hydrogenation to methanol is modeled using a kinetic approach based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, employing the Van-Dal and Bouallou (2013) kinetic model, which was previously adapted by recalculating the driving force and adsorption coefficients to fit Aspen Plus requirements The kinetic model parameters for bi-reforming has been taken from the work of (Nguyen and Zondervan, 2019).

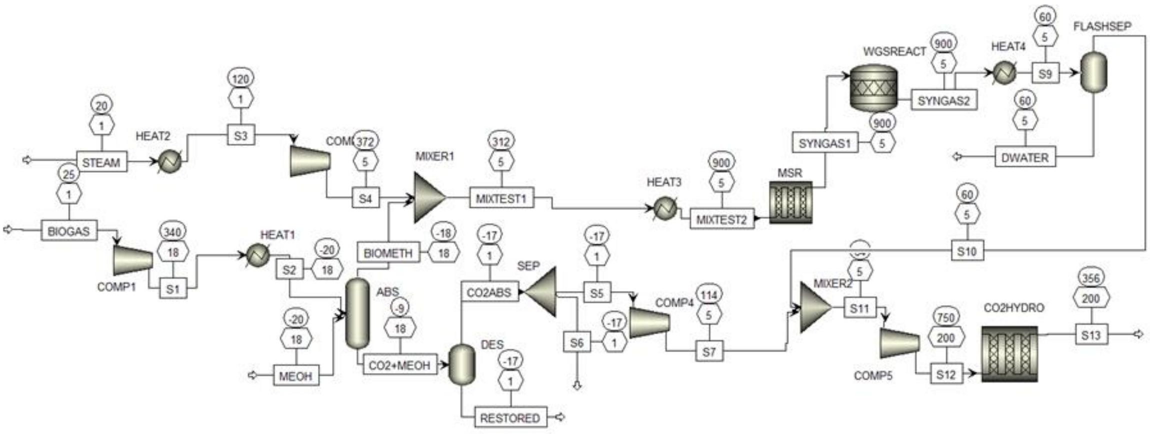
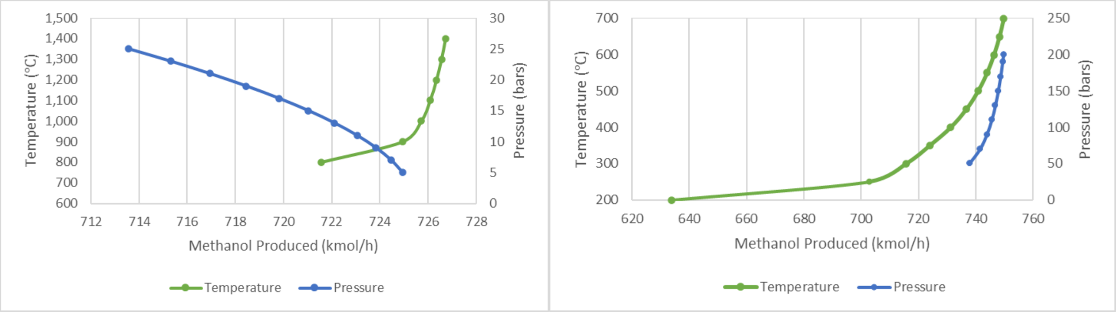


Figure 1: Simulation process with stream temperature (in circles) and pressure (in hexagons)

The process begins with biogas, composed primarily of 60 % CH_4 and 40 % CO_2, and steam as inputs. In this study, 1,000 kmol/hr of biogas and 4,000 kmol/hr of steam are fed into the system. The biogas is first compressed to 18 bars and then cooled down to –20 °C before entering the CO_2 separation adsorption column, where CO_2 is removed using methanol as the absorbent. The cold biogas enters an absorption column (ABS) where physical CO_2 absorption occurs with chilled methanol according to Henry's Law, producing a CO_2-rich stream (CO_2+MEOH) and a methane-rich stream (BIOMETH). The CO_2-rich stream is then sent to a desorption column to separate the CO_2 from the methanol for recirculation. In the bi-reforming stage, the methane-rich stream is mixed with additional steam and heated up to 900 °C. This mixture enters the Reforming Reactor, which is modeled as a plug flow reactor (PFR) using bi-reforming kinetics and operating conditions taken from (Nguyen and Zondervan, 2019). *The reactor* consists of 10 tubes, each 10 m long with a diameter of 10.16 cm, packed with a Ni-CeO_2/$MgAl_2O_4$ catalyst, bed voidage of 0.605, and particle density of 2,396.97 kg/m^3. Here, bi-reforming occurs to produce syngas (CO_2, CO, and H_2). The syngas then flows into a water-gas shift (WGS) reactor, which is modeled in Aspen Plus v12.1 as a stoichiometric reactor operating at 900 °C and 5 bar, with a 100 % conversion assumption to convert CO into additional CO_2 and H_2. The shifted syngas, rich in CO_2 with no remaining CO, enters a flash separator to remove excess water. The dry syngas is then mixed with additional CO_2 recovered from the biogas to achieve the desired H_2/CO_2 ratio of approximately 3 for the CO_2 hydrogenation step. This mixture is compressed to 200 bars before entering the CO_2 Hydrogenation Reactor, which is also modeled as a kinetics plug flow reactor. This reactor consists of 10,000 tubes, each 12.2 m long with a diameter of 0.375 m, filled with a Cu/ZnO/Al2O3 commercial catalyst, having a bed voidage of 0.4 and a particle density of 2,000 kg/m^3 (Van-Dal and Bouallou, 2013). The reactor operates at 750 °C, where CO_2 direct hydrogenation takes place over the catalyst, producing methanol.

5.2 Sensitivity analysis

To optimize this process, sensitivity analyses were conducted to evaluate the impact of key variables on methanol production.



(a) *(b)*

Figure 2: Methanol production (kmol/h) vs. temperature (°C) and pressure (bars) for (a) MSR and (b) CO_2 Hydrogenation

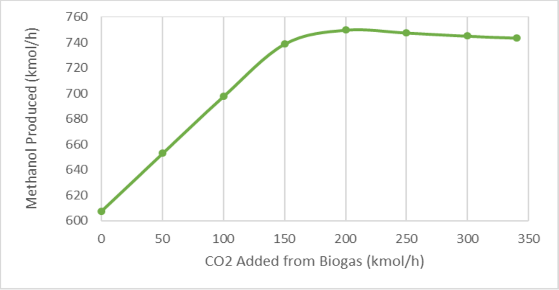


Figure 3: Methanol production (kmol/h) vs. CO2 added from biogas (kmol/h)

Table 1: Composition of main streams in the process simulation

Stream name	Units	BIOGAS	BIOMETHANE	CO_2+MEOH	MIXT2	SYNGAS1	S6	SYNGAS2	S12	S13
Mole-flow	kmol/h	1,000	609.04	3,391	4,609	5,749	133.0	5,749	3,196	1,701
CH_4		0.6	0.93	0.008	0.12	-	0.09	-	-	17.94
CO_2		0.4	0.06	0.106	0.008	0.06	0.9	0.1	0.25	19.32
CO		-	-	-	-	0.05	-	-	-	21.70
H_2O		-	-	-	0.87	0.5	-	0.5	0.03	876.75
H_2		-	-	-	-	0.35	-	0.4	0.71	15.38
CH_3OH		-	-	0.88	-	-	-	-	-	749.72

Sensitivity analysis were performed to evaluate the impact of key operating variables on methanol production, including the reforming reactor temperature and pressure, the methanol synthesis reactor temperature and pressure, and the amount of CO_2 added from biogas. The process model was run in Aspen Plus V12.1, systematically varying each parameter within realistic industrial ranges while holding other variables constant, to identify trends, optimal conditions, and possible trade-offs for maximizing methanol yield.

5.3 Technical and environmental analysis

Single-pass conversion for CO_2 in methanol reactor (Eq(6)):

$$X_{CO2} = \frac{F_{CO2}^{in} - F_{CO2}^{out}}{F_{CO2}^{in}} = \frac{788.816 - 6.074}{788.816} = 99.22\ \% \tag{6}$$

Overall process conversion for CO_2 (Eq(7)):

$$X_{CO2}^{overall} = \frac{F_{CO2}^{feed} - F_{CO2}^{product} - F_{CO2}^{purge}}{F_{CO2}^{feed}} = \frac{400 - 6.074 - 180.733}{400} = 53.29\ \% \tag{7}$$

Product yield for methanol with respect to the biogas feed (Eq(8)):

$$\eta_{CH3OH}^{biogas} = \frac{F_{CH3OH}^{out}}{F_{biogas}^{in}} = \frac{724.948}{1000} = 72.49\ \% \tag{8}$$

Product yield for methanol with respect to the CO_2 feed (Eq(9)):

$$\eta_{CH3OH}^{CO2} = \frac{F_{CH3OH}^{out}}{F_{CO2}^{in}} = \frac{724.948}{400} = 181.23\ \% \tag{9}$$

Net direct CO_2 emission calculated by Eq(10) (The input and output streams include CO_2 were taken from the simulation for the calculation):

$$n_{emitted}^{CO2} = (CO_2)^{out} - (CO_2)^{in} = (CO_2)^{S6} + (CO_2)^{S13} - (CO_2)^{Biogas} = -260.52\ kmol/h \tag{10}$$

Conversion ratios of CH_4, CO and CO_2 are high. It should be taken into consideration in the overall process conversion that the CO_2 in the purge feed originates from the atmosphere, as it is part of a closed carbon cycle loop and therefore this is not technically considered a direct CO_2 emission.

6. Results and discussion

Figure 2a shows that methanol production increases with higher reforming reactor temperatures, rising from about 721 kmol/h at 720 °C to nearly 727 kmol/h at 1,400 °C, consistent with the fact that reforming reactions (e.g., steam methane reforming, dry reforming) are highly endothermic and favored by higher temperatures, which enhance the conversion of feedstocks into syngas (H_2 and CO/CO_2) for methanol synthesis. Conversely, the graph indicates an inverse relationship between reforming reactor pressure and methanol production within this temperature range, with the optimal pressure decreasing from around 25 bar to approximately 5 bar as methanol production increases. Figure 2b shows that methanol production strongly depends on both the temperature and pressure within the methanol synthesis reactor. As the reactor temperature increases from about 200 °C to 700 °C, methanol production rises significantly from roughly 635 kmol/h to nearly 750 kmol/h, indicating that higher temperatures enhance reaction kinetics and boost yield. Likewise, increasing the pressure from around 50 bar to 200 bar further raises methanol production from about 735 kmol/h to 750 kmol/h, which aligns with Le Chatelier's principle since methanol synthesis reduces total gas moles, favoring high pressures. Overall, the results demonstrate that operating the methanol synthesis reactor at both elevated temperatures and pressures is essential for maximizing production, with optimal conditions in this range appearing around 700 °C and 200 bar to achieve production rates above 740 kmol/h.

The objective of this sensitivity analysis in Figure 3, was to determine the optimal amount of CO_2 to add from biogas to maximize methanol production, given its role as a renewable carbon source. The graph shows that increasing the CO_2 feed initially boosts methanol production sharply, from about 600 kmol/h with no added CO_2 to a peak of around 750 kmol/h at approximately 200 kmol/h of added CO_2. Beyond this point, production plateaus or slightly declines, suggesting that further CO_2 addition offers little benefit and may even reduce output due to stoichiometric limitations (e.g., insufficient hydrogen), possible shifts in reaction equilibrium, or dilution effects from excess CO_2 or inert gases. This indicates that the optimal CO_2 addition from biogas is around 200 kmol/h, which maximizes methanol yield without unnecessary excess. This insight is important for process design, as it confirms the value of CO_2 from biogas as a sustainable feedstock while highlighting that exceeding the optimal point could raise separation costs or negatively impact catalyst performance without improving production. The single-pass CO_2 conversion, overall CO_2 conversion, and product yields were calculated using Eqs(6)–(9). For the base case, the single-pass CO_2 conversion in the methanol reactor is 99.22 %, while the overall CO_2 conversion for the process is 53.29 %. The product yield with respect to the total biogas feed is

72.49 %, while the yield with respect to the CO_2 feed alone is 181.23 %. This apparent yield above 100 % occurs because the process uses both CO_2 and CH_4 as carbon sources: CH_4 is reformed to syngas ($CO + H_2$), which is then hydrogenated with CO_2 to methanol, increasing the total methanol output beyond the stoichiometric contribution of CO_2 alone.

Based on the data from Table 1, for a methanol production of 749.72 kmol, a total of 139.48 kmol of CO_2 is emitted back into the atmosphere. While the biogenic methanol production process emits 255.52 g of CO_2 per kg of methanol, this CO_2 is derived from renewable sources like biogas, making it part of the natural carbon cycle. In contrast, the traditional process using natural gas emits 110 g of fossil CO_2 per kg of methanol, contributing to long-term atmospheric CO_2 accumulation. Though the biogenic process emits more CO_2, it is a sustainable alternative that avoids fossil fuel reliance and reduces net emissions over time.

7. Conclusion

This study successfully models and simulates an innovative, integrated process for methanol production from biogas in Aspen Plus V12.1, offering a promising solution for reducing carbon intensity and achieving carbon-negative emissions. The process effectively integrates CO_2 and CH_4 separation, hydrogen production through bi-reforming, and methanol synthesis via CO_2 hydrogenation. The results indicate that this approach can significantly reduce carbon emissions compared to conventional methanol production from fossil fuels. This work provides an important basis for future investigations on process optimization, operability, controllability, and sustainability assessments for large-scale, low-carbon methanol production from biogas.

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