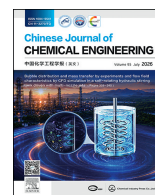




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## Full Length Article

## Comparative techno-economic and environmental assessment of hydrogen-to-carbon ratio adjustment strategies in biogas to methanol processes

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## ABSTRACT

This study investigates biogas as a renewable feedstock for green methanol production and compares three hydrogen-to-carbon (H/C) ratio adjustment strategies: (I) CO<sub>2</sub> removal before reforming, (II) CO<sub>2</sub> removal after reforming, and (III) green hydrogen supplementation. Each route is evaluated using high-fidelity process simulations, techno-economic analysis, and life cycle assessment. Route II achieves the lowest minimum selling price (419 USD·t<sup>-1</sup> at a capacity of 100 kt·a<sup>-1</sup>) and lowest net greenhouse gas (GHG) emissions (144 kg CO<sub>2</sub> per tonne of methanol), due to superior energy efficiency and carbon utilization. Route III offers the highest production yield but depends heavily on low-cost green hydrogen. Our findings identify optimal pathways for deploying biogas-to-methanol technologies under varying economic and policy conditions.

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## 1. Introduction

Methanol, a key chemical feedstock and energy carrier, is widely used in fuels, chemical synthesis, and hydrogen storage [1]. Conventional methanol production heavily relies on fossil fuels, particularly coal and natural gas, leading to significant CO<sub>2</sub> emissions [2]. On average, producing one tonne of methanol emits 2.5 to 3 tonnes of CO<sub>2</sub>, posing a challenge to its long-term sustainability [3]. Green methanol, defined as methanol synthesized from renewable resources via low-carbon pathways such as biomass, CO<sub>2</sub> utilization, and green hydrogen, has emerged as a promising alternative [4]. It achieves very low CO<sub>2</sub> emissions throughout its life cycle and is expected to play a critical role in future energy systems [5,6]. The International Energy Agency (IEA) predicts that by 2050, green methanol could account for over 60% of the global methanol supply, serving as a renewable fuel, energy carrier, and

carbon-based platform chemical [7]. In the maritime sector, the demand for green methanol is steadily increasing as the shipping industry seeks to reduce its carbon emissions [8,9]. A.P. Møller–Maersk, one of the largest and most influential shipping companies globally, for example, has ordered 24 dual-fuel container ships capable of running on green methanol, with deliveries between 2024 and 2027. These vessels are projected to consume 200–250 t of methanol per day, highlighting the rapidly emerging market for marine methanol, which is expected to grow into the multi-million-tonne range annually [10]. Beyond environmental benefits, green methanol offers strong economic potential. While fossil-derived gray methanol typically sells for 300–400 USD·t<sup>-1</sup>, green methanol can reach 600–900 USD·t<sup>-1</sup>, indicating both a growing premium and a market shift toward sustainable fuels [11,12]. Developing efficient, scalable production pathways is thus crucial to enhance its competitiveness.

Among various renewable carbon sources, biogas stands out as an especially attractive feedstock for green methanol production due to its abundant availability and high content of both methane and carbon dioxide [13,14]. In major markets like China, the potential biogas production is substantial—approximately 200 billion cubic meters per year [15–17]. Converting biogas to green

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methanol not only adds economic value but also mitigates methane leakage, offering both economic and environmental benefits [18]. Converting biogas to methanol involves four fundamental steps: biogas pre-treatment to remove contaminants such as hydrogen sulfide; converting cleaned biogas into syngas through bi-reforming, which is a combination of steam reforming and dry reforming; adjusting the hydrogen-to-carbon (H/C) ratio; and methanol synthesis (the detailed descriptions of those chemical processes are introduced in the next section) [19,20]. Different from natural gas reforming, using biogas, which contains high levels of  $\text{CO}_2$ , requires additional steps to adjust the H/C ratio. This is because the typical composition of raw biogas—approximately 30% to 50%  $\text{CO}_2$ —results in a syngas mixture with a low  $\text{H}_2/\text{CO}$  ratio when reformed, which is not well-aligned with the stoichiometric requirements for methanol synthesis. In particular, methanol production via  $\text{CO}$  and  $\text{CO}_2$  hydrogenation requires a specific balance of hydrogen to carbon oxides, which is difficult to achieve with biogas-derived syngas unless the  $\text{CO}_2$  content is reduced or hydrogen is added. Excess  $\text{CO}_2$  dilutes the reformer feed, lowers hydrogen yield, and increases the hydrogen demand downstream, ultimately reducing reactor productivity and increasing energy and capital requirements. As such, adjusting the H/C ratio through  $\text{CO}_2$  removal or  $\text{H}_2$  supplementation is a critical process design consideration when utilizing biogas as a feedstock for sustainable methanol production [21,22]. A block flow diagram illustrating the three different H/C ratio adjustment strategies is shown in Fig. 1. The  $\text{CO}_2$  is either removed before or after reforming process to adjust H/C ratio [23,24]. Alternatively, instead of removing excess  $\text{CO}_2$ , one can supplement additional green hydrogen to tune the H/C ratio and make the most use of carbon [25].

Each of these approaches presents distinct technical and economic trade-offs. In the first route, a portion of the  $\text{CO}_2$  is removed prior to reforming to tune the feed composition toward a desirable  $\text{H}_2/\text{CO}$  ratio. This adjustment is intended not to fully utilize biogas but to bring the reformer feed closer to the optimal synthesis gas composition for methanol production. For example, Moioli and Schildhauer [26] examined the techno-economic performance of biogas reforming systems where partial  $\text{CO}_2$  removal is applied to meet stoichiometric synthesis conditions. They showed that this strategy can be economically attractive, particularly at small scales, though it requires additional separation units and may underutilize some of the biogenic carbon. The second strategy avoids  $\text{CO}_2$  separation upfront by retaining it in the reformer feed to generate syngas with a tunable  $\text{H}_2/\text{CO}$  ratio. Schiaroli *et al.* [27] demonstrated that bi-reforming using clean biogas as both feed and energy source can achieve syngas compositions suitable for methanol synthesis, with a favorable environmental profile and net-negative  $\text{CO}_2$  emissions under certain conditions. Hernández

and Martín [28] developed a detailed process optimization framework for this route and found that methanol production can be economically viable without prior  $\text{CO}_2$  removal, particularly when mild steam addition is used to suppress carbon deposition and facilitate heat integration. The third route involves supplementing syngas with external green hydrogen to adjust the H/C ratio directly, thereby enabling full utilization of the carbon content in both  $\text{CH}_4$  and  $\text{CO}_2$ . This strategy aligns with power-to-X principles and is particularly attractive in regions with abundant renewable electricity [29]. Moioli and Schildhauer [26] showed that methanol yield can be significantly enhanced with hydrogen supplementation, and under favorable electricity prices, this approach becomes economically competitive. However, it increases process complexity and requires precise thermal integration between electrolyzers, reformers, and synthesis loops [30]. Despite growing interest in each pathway, the literature lacks a systematic, side-by-side comparison under consistent boundary conditions. Most existing studies focus on a single strategy and evaluate performance using different assumptions regarding plant scale, heat integration, or reaction conditions. Furthermore, high-fidelity simulations that integrate reaction kinetics, heat recovery, recycle handling, and environmental accounting remain scarce. Our work addresses this gap by developing a comparative framework across the three H/C adjustment strategies for methanol production from biogas, spanning capacities from 10 to 100 kilotonnes per year. We incorporate detailed process modeling, heat integration, techno-economic analysis, and life cycle assessment to evaluate carbon utilization, energy efficiency, cost-effectiveness and environmental benefits. This integrated analysis provides insights into which pathway is most appropriate under various technological, economic, and policy constraints. The rest of paper is organized as follows: we first introduce the detailed chemical processes involved. We then compared and analyzed three routes in terms of carbon efficiency, energy efficiency, cost effectiveness and environmental benefits. At the end of the paper, we also discussed the future works that could further improve the efficiency of biogas to methanol process.

## 2. Process Description

In this study, biogas produced by a wastewater treatment plant run by Sinopec in Shanghai via anaerobic digestion of wastewater sludge is analyzed for methanol production. It should be acknowledged that biogas composition can vary significantly depending on the feedstock and digestion conditions. Therefore, this specific composition is adopted as a representative baseline to facilitate a consistent comparative analysis of the three H/C ratio adjustment strategies. The detailed gas composition can be found in the Supplementary Material. All three routes share a common

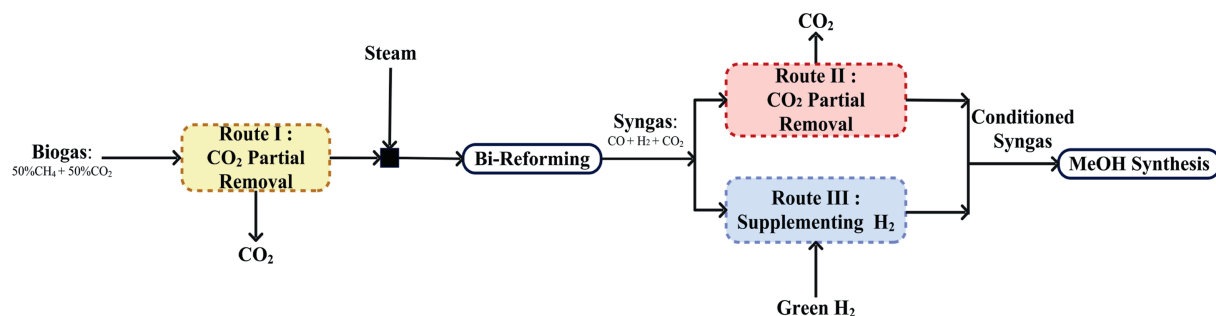
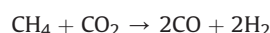
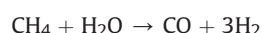


**Fig. 1.** Schematic diagram of three biogas-to-methanol routes. Three processing routes are proposed and compared for optimizing syngas compositions for efficient methanol synthesis. Route I: Partial  $\text{CO}_2$  removal from biogas before bi-reforming. Route II: Partial  $\text{CO}_2$  removal from the bi-reforming product stream to adjust syngas composition. Route III: Supplemental  $\text{H}_2$  introduced to the bi-reforming product stream to tune syngas composition.

backbone consisting of biogas pretreatment, bi-reforming, syngas cooling and conditioning, methanol synthesis, and distillation. Raw biogas is first desulfurized and dried.  $\text{H}_2\text{S}$  and other trace contaminants are removed to protect the downstream catalysts [31,32]. A portion of the biogas is diverted as fuel for the reformer furnace. The remaining biogas is then mixed with steam and preheated before entering the reformer. The outlet syngas is cooled using waste heat recovery and separated from condensed water. After conditioning and compression, the syngas enters a fixed-bed methanol synthesis reactor operating at  $\sim 220^\circ\text{C}$  and 6 MPa. The reactor effluent is cooled, phase-separated, and sent to a two-column distillation system for methanol purification. Unreacted gases are recycled, while purge streams are either recovered or used as furnace fuel.

**Bi-Reforming:** The reformer is designed as an externally fired tubular reactor performing combined steam and dry reforming reactions [33]:



The reactor operates at  $910^\circ\text{C}$  and 1 MPa, with heat supplied by combustion of a side stream of biogas and/or purge gas. Specifically, an overall thermal efficiency of 90% (equivalent to 10% thermal loss) is assumed for the reformer furnace [34]. The energy from purge gas combustion is recovered based on its lower heating value (LHV) and fully credited toward the furnace duty in the

radiant section, thereby offsetting the demand for primary biogas fuel. This approach accurately reflects the net energy balance and contributes to the calculated carbon efficiency by minimizing external fuel consumption. Air is preheated in the convective section and fed to the burner, producing flue gas with  $\sim 4\%$ (mol) residual oxygen. The steam-to-carbon (S/C) ratio, defined as the molar ratio of  $\text{H}_2\text{O}$  to  $\text{CH}_4$  [35], ranges between 1.8 and 2.5 across three routes, ensuring sufficient hydrogen generation while suppressing carbon formation. The optimal S/C varies by routes depending on feed  $\text{CO}_2$  content, as lower  $\text{CO}_2$  requires higher S/C to keep the consistent methane conversion.

**Route I –  $\text{CO}_2$  Removal Before Reforming:** As shown in Fig. 2, a fraction of  $\text{CO}_2$  is removed prior to reforming using a methyl-diethanolamine (MDEA)-based chemical absorption system [36]. This partial decarbonization enriches the methane concentration in the feed and raises the H/C ratio. After treatment, the biogas typically contains  $\sim 28\%$ (mol)  $\text{CO}_2$ , reduced from  $\sim 40\%$  to  $45\%$ (mol) in raw biogas. The treated biogas is mixed with steam and sent to the reformer. As less  $\text{CO}_2$  is present in the feed, the reforming reactions produce a hydrogen-rich syngas. After cooling, the syngas generally meets the required stoichiometric module ( $M \approx 2.05$ ) for methanol synthesis, defined as [37]:

$$M = \frac{(X_{\text{H}_2} - X_{\text{CO}_2})}{(X_{\text{CO}} + X_{\text{CO}_2})}$$

In the Aspen Plus simulation, a Design Spec block is implemented to dynamically adjust the MDEA solvent circulation rate,

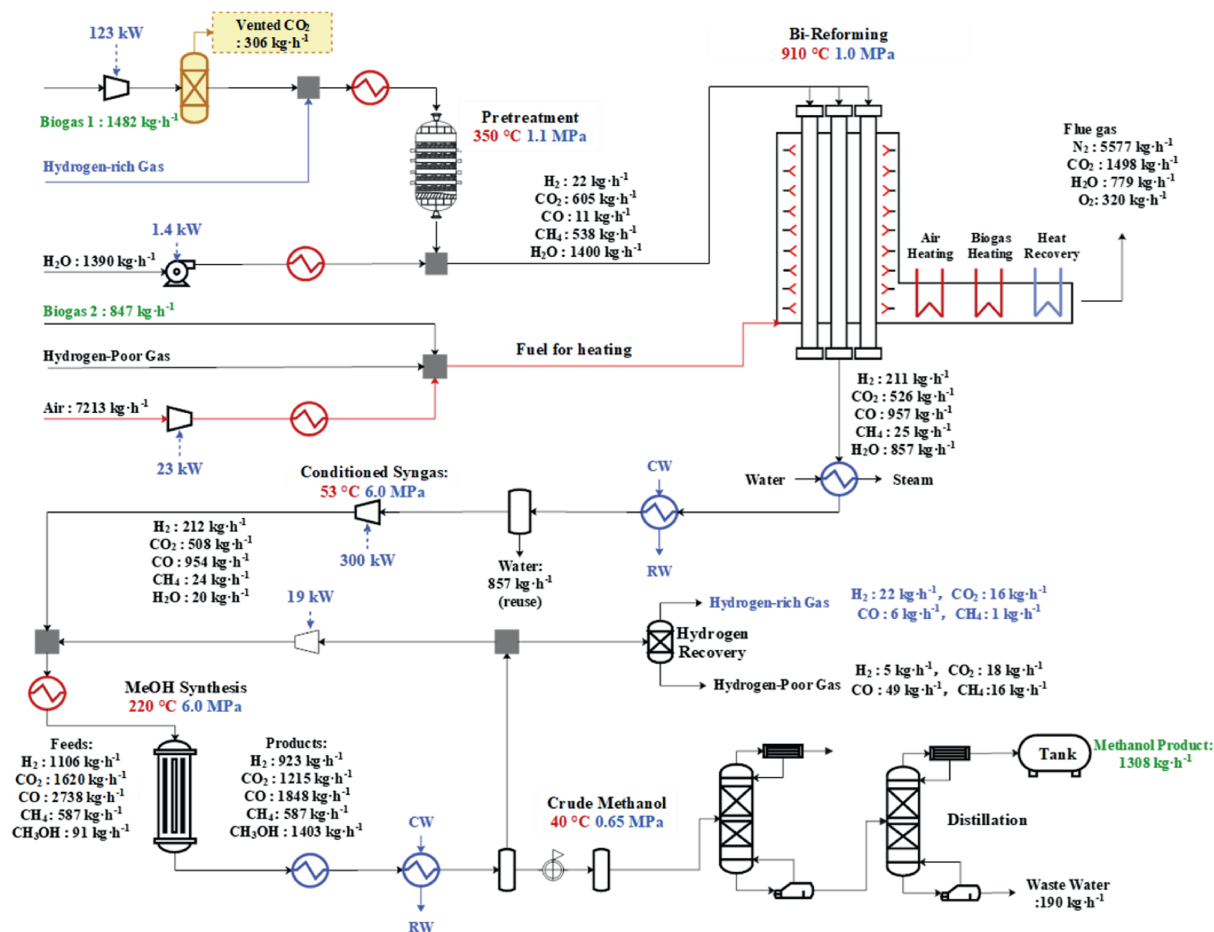


Fig. 2. Process flowsheet of Route I. A portion of  $\text{CO}_2$  is removed before reforming to adjust the H/C ratio. The conditioned biogas yields a hydrogen-rich syngas suitable for methanol synthesis without further modification.

ensuring the conditioned syngas precisely achieves this target stoichiometric module. No further H/C adjustment is needed. This route simplifies downstream processing by eliminating the need for a shift reactor or post-reforming CO<sub>2</sub> removal. However, higher S/C ratio requirements increase energy consumption, while some biogenic CO<sub>2</sub> is discarded resulting in lower carbon utilization.

**Route II – CO<sub>2</sub> Removal After Reforming:** as shown in Fig. 3, the raw biogas, containing both CH<sub>4</sub> and CO<sub>2</sub>, is directly sent to the reformer after pretreatment, without any CO<sub>2</sub> removal beforehand. Due to the high CO<sub>2</sub> content in the feed, the reformat tends to have a lower H<sub>2</sub>/CO ratio and higher CO<sub>2</sub> content compared to Route I. To adjust the H/C ratio for methanol synthesis, this configuration performs CO<sub>2</sub> removal after reforming. After heat recovery and condensation, the syngas is cooled and sent to a chemical absorption unit using an MDEA–water solvent. The scrubber operates at elevated pressure (~1 MPa) and removes a controlled fraction of CO<sub>2</sub> to bring the stoichiometric module (*M*) close to the target of ~2.05. Similar to Route I, the CO<sub>2</sub> removal fraction is controlled by a Design Spec block that modulates the MDEA solvent circulation rate until the downstream syngas composition reaches the target stoichiometric module.

**Route III – Hydrogen Supplementation:** Route III (Fig. 4) does not remove CO<sub>2</sub> at any stage. Instead, it supplements the reformat with external green hydrogen to elevate the H/C ratio. After bi-reforming, the low-H<sub>2</sub> syngas is blended with electrolytic hydrogen (produced from water electrolysis) [38], raising the syngas composition to the required stoichiometric module. This

strategy enables complete utilization of biogenic CO<sub>2</sub>, maximizing carbon efficiency and eliminating the need for CO<sub>2</sub> separation. However, the energy and cost of hydrogen production must be considered. The increased water content from CO<sub>2</sub> hydrogenation also leads to higher load on the separation system.

**Methanol Synthesis and Separation:** Before entering the methanol synthesis loop, the conditioned syngas is compressed and combined with recycled gas. Water condensed from syngas cooling is collected and recycled to generate steam, which is mixed with biogas at the reformer inlet. In all configurations, the conditioned syngas is compressed to 6 MPa and introduced into a tubular fixed-bed reactor operating at ~220 °C [39]. The exothermic reactions convert CO and CO<sub>2</sub> with H<sub>2</sub> into methanol and water. The reactor includes internal cooling to maintain isothermal conditions and avoid temperature hotspots. The reactor effluent is cooled and passed through a flash separator. The liquid phase (crude methanol + water) is sent to a two-column distillation system. The first column removes light ends; the second separates methanol from water. The final product is 99.99%(mol) pure methanol. Recycle loops and purge streams are implemented to maintain stable operation. Purge gases are utilized as fuel for the reformer, recovering energy and reducing emissions. The hydrogen-rich gas, recovered via membrane separation from the purge stream, is recycled to the biogas pretreatment process. Hydrogen-poor gas is combusted in the reformer furnace to improve energy efficiency. This integrated heat and material recovery system minimizes utility demand and ensures the hydrogen demand of biogas pretreatment for removing impurities like O<sub>2</sub> and organic sulfide [40].

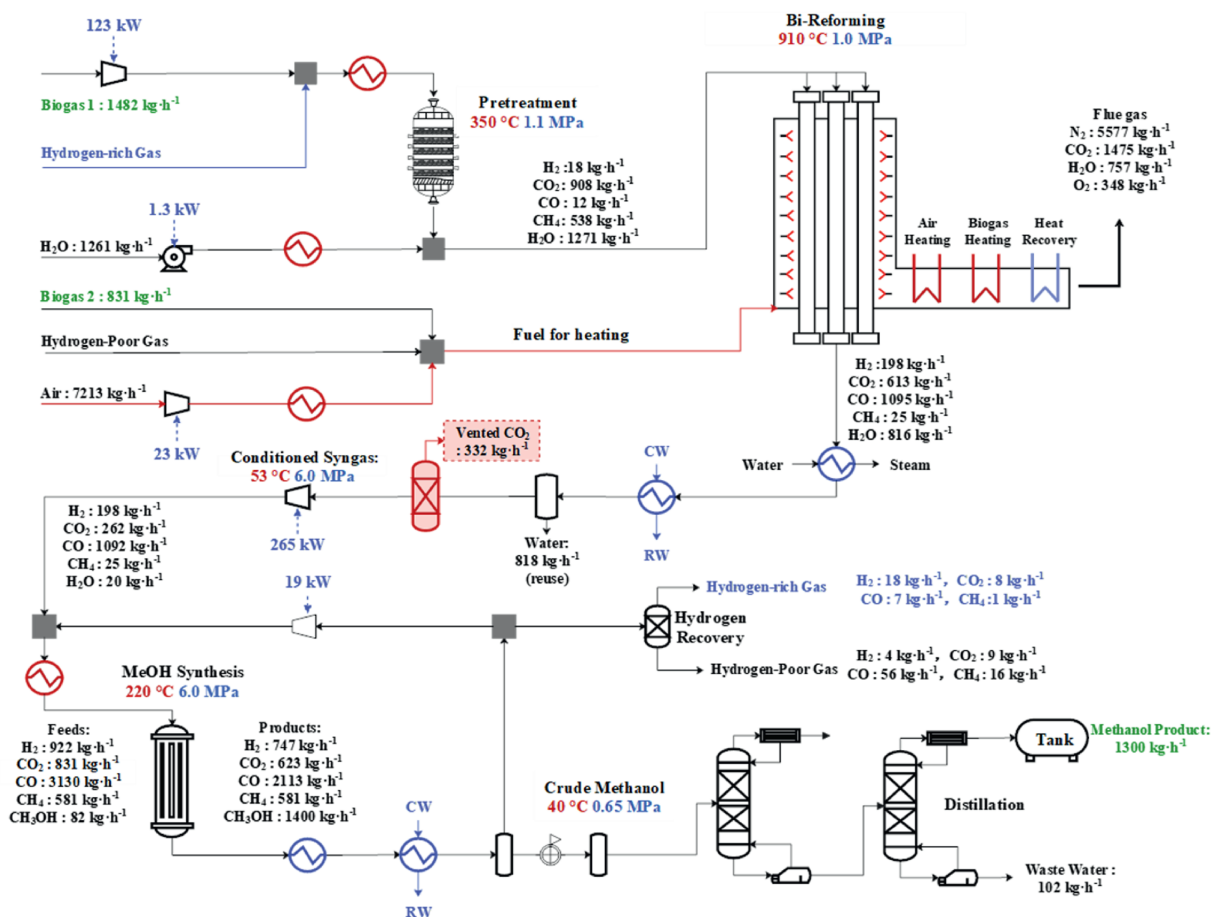


Fig. 3. Process flowsheet of Route II. Biogas reforming is followed by a post-reforming CO<sub>2</sub> removal to adjust the H/C ratio.

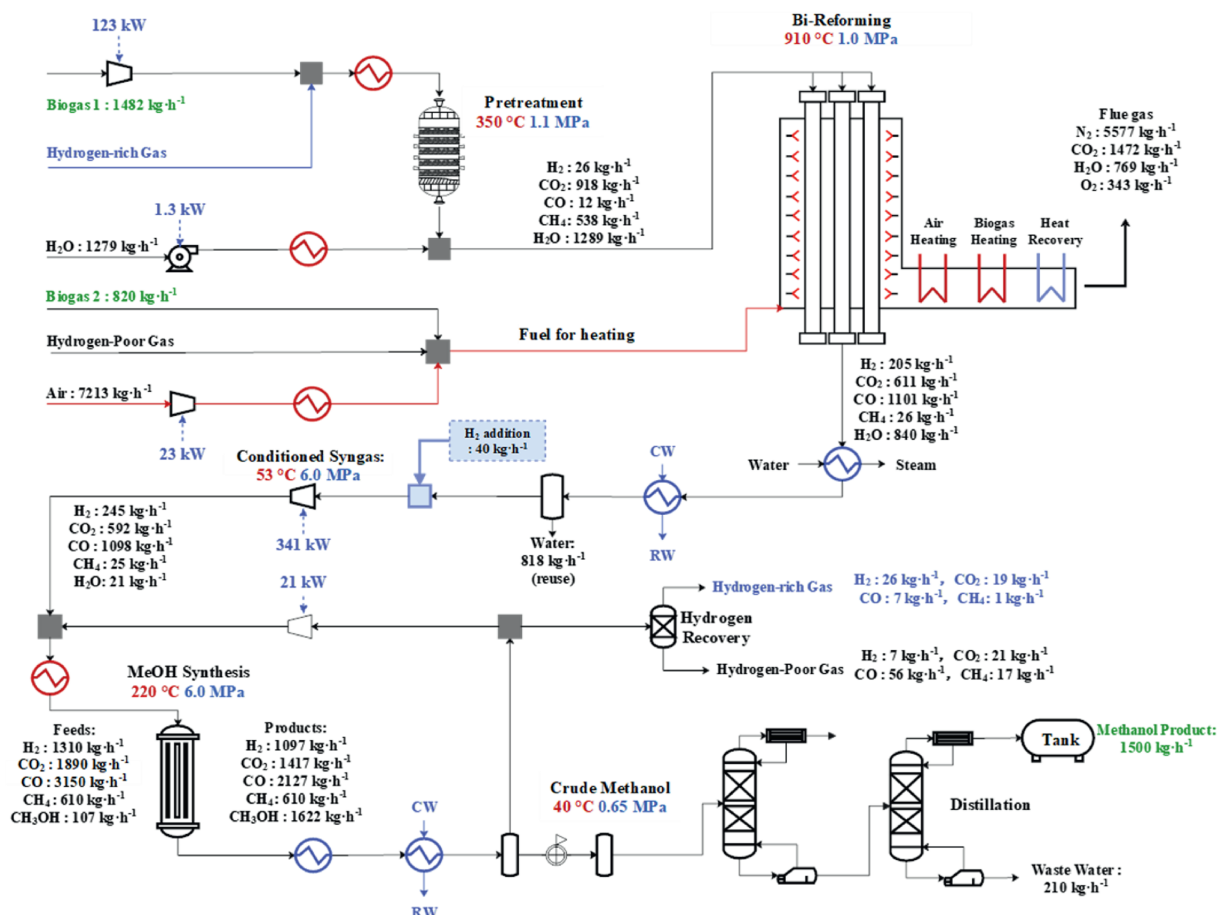


Fig. 4. Process flowsheet of Route III. Instead of removing partial CO<sub>2</sub> from biogas or reformat streams, green hydrogen is added tune the syngas composition.

### 3. Results and Discussion

We perform high fidelity process simulations for three production routes using Aspen Plus V14. We also use Aspen Energy Analyzer to conduct the heat integration to further intensify the energy efficiency of the overall process. For the pinch analysis, a minimum temperature approach of 10 °C was specified. This value aligns with typical industrial practices for syngas conditioning and methanol synthesis. It ensures a practical techno-economic balance by maximizing waste heat recovery to reduce utility expenses, while maintaining the required heat exchanger surface areas and overall capital costs within reasonable limits. Detailed parameters, including operating conditions, capital cost, operating cost and carbon footprints of key processing units are provided in Supplementary Material.

#### 3.1. Mass and energy balance

To isolate the specific effects of each route on process performance, we maintain consistent values for several key operational variables across all configurations. We first fix the methane conversion rate of 95.4% across all three processing routes by tuning the amount of steam fed to the reformer. This methane conversion rate is the highest under high-temperature reforming conditions we have observed from existing Sinopec's industrial plants. This fixed target serves primarily as a rigorous benchmarking baseline to ensure a fair, apples-to-apples comparison of the distinct H/C ratio adjustment strategies, rather than an individually optimized operating point for each route. While minor deviations around this

target through individual process optimization might cause slight variations in specific reformer heat duties and utility consumption, our preliminary assessments indicate that such deviations would not alter the overall comparative trends nor the final economic ranking of the three configurations. We maintain the stoichiometric module (*M*) of the fresh gas feed at 2.05 for methanol synthesis reaction. Additionally, under our current industrial operating conditions, the inert gas content in the inlet gas remains below 12%, and the purge gas ratio is set at 3% to prevent the accumulation of inert gases in the methanol synthesis loop.

The methanol production rates of the first two routes are nearly identical (see Table 1). Because a portion of CO<sub>2</sub> is removed before the reformer in Route I, less CO<sub>2</sub> participates in the reforming reaction compared to Route II. To maintain the same methane conversion rate, we set the steam-to-carbon (S/C) ratio at 2.32 for Route I, while Route II only requires 2.11. Since biogas reforming is strongly endothermic, the higher S/C ratio demands greater thermal input, requiring more biogas combustion to meet the reactor's heat demand. For Route I, producing 1 kg of MeOH requires burning 1.79 kg of biogas for reformer heating. This results in lower carbon utilization efficiency (defined as the fraction of biogas carbon atoms converted to methanol) – 52.4% for Route I versus 53.1% for Route II. The exergy efficiency follows the same trend (Route I: 69.2%; Route II: 71.2%), which is defined as the ratio of the useful chemical exergy in methanol product to the total exergy input from biogas, supplemental hydrogen, and other utilities [41]. Further details on the calculation methods and assumptions for both carbon efficiency and exergy efficiency can be found in the Supplementary Material.

**Table 1**  
Plant-level mass and energy balances of three processing routes.

| Items                                         | Unit               | Route I | Route II | Route III |
|-----------------------------------------------|--------------------|---------|----------|-----------|
| <b>Mass balance</b>                           |                    |         |          |           |
| MeOH production rate                          | kg·h <sup>-1</sup> | 1304    | 1306     | 1507      |
| Biogas consumption (per kg methanol)          | kg                 | 1.79    | 1.74     | 1.54      |
| CO <sub>2</sub> removal (per kg methanol)     | kg                 | 0.24    | 0.25     | —         |
| H <sub>2</sub> supplemented (per kg methanol) | kg                 | —       | —        | 0.027     |
| LP steam surplus (per kg methanol)            | kg                 | 0.88    | 0.94     | 0.82      |
| Deionized water consumption (per kg methanol) | kg                 | 1.51    | 1.43     | 1.48      |
| <b>Biogas reformer</b>                        |                    |         |          |           |
| S/C ratio                                     | —                  | 2.32    | 2.11     | 2.13      |
| CH <sub>4</sub> conversion rate               | %                  | 95.4    | 95.4     | 95.4      |
| <b>MeOH synthesis</b>                         |                    |         |          |           |
| Stoichiometric module                         | —                  | 2.05    | 2.05     | 2.05      |
| Inert gas                                     | %                  | 9.5     | 10.8     | 8.3       |
| Purge gas ratio                               | %                  | 3.0     | 3.0      | 3.0       |
| Recycle ratio                                 | —                  | 3.91    | 3.52     | 3.95      |
| Carbon efficiency                             | %                  | 52.4%   | 53.1%    | 56.2%     |
| Exergy efficiency                             | %                  | 69.2%   | 71.2%    | 70.8%     |
| <b>Energy balance</b>                         |                    |         |          |           |
| Biogas compressor                             | kW                 | 160.9   | 160.9    | 160.9     |
| Reformer pump                                 | kW                 | 1.4     | 1.1      | 1.2       |
| Syngas compressor                             | kW                 | 363.0   | 345.2    | 444.2     |
| Recycle gas compressor                        | kW                 | 24.0    | 20.5     | 27.9      |
| Air fan                                       | kW                 | 23.1    | 23.1     | 23.1      |
| MDEA pump                                     | kW                 | 3.0     | 4.0      | —         |
| Pumps in heat recovery system                 | kW                 | 17.7    | 17.6     | 17.7      |
| Total power consumption                       | kW                 | 593.1   | 572.4    | 675.0     |
| Unit power consumption (per kg methanol)      | kW·h               | 0.455   | 0.438    | 0.448     |

Steam generation and utilization are key factors affecting the overall process energy efficiency. There are two primary heat sources to generate the steam: first, from the sensible heat recovered from high-temperature flue gases and the overheated syngas from the reformer outlet, and second, from the reaction heat released during methanol synthesis (indirectly generating steam via a boiling water-cooling system). The steam is mainly used to provide heat for the reboiler of the crude methanol distillation column. Additionally, in both Route I and Route II, the MDEA regeneration tower in the CO<sub>2</sub> removal unit also consumes steam to drive the desorption process. Based on our process simulations, the specific reboiler duty required for solvent regeneration is quantified at approximately 3.10 MJ per kg CO<sub>2</sub> captured for Route I, and 3.72 MJ per kg CO<sub>2</sub> captured for Route II. This higher specific energy consumption in Route II is thermodynamically expected due to the lower CO<sub>2</sub> partial pressure in the post-reforming syngas. However, despite this higher local steam consumption in the CO<sub>2</sub> removal unit, Route II ultimately yields a higher net surplus of low-pressure steam overall. This is because the post-reforming carbon removal strategy allows the reformer to operate at a lower steam-to-carbon ratio, drastically reducing the high-pressure steam demand upstream and resulting in a more favorable plant-wide steam balance (see Table 1). Furthermore, steam is used in the catalytic hydrodeoxygenation reaction in the biogas pretreatment unit to maintain the reaction temperature and improve catalyst stability. After satisfying internal heat demands, the system exports residual low-pressure steam for external processes or heat recovery. Following heat integration, Route I produces 0.88 kg and Route II yields 0.94 kg of surplus low-pressure steam per kilogram of methanol.

Unsurprisingly, Route III achieves the highest methanol production rate among the three configurations, with the lowest biogas consumption per unit of methanol production (1.54 kg biogas per kg MeOH), due to the supplemental hydrogen input. The hydrogen supplementation allows for precise adjustment of the stoichiometric ratio of the syngas ( $M = 2.05$ ) without the need for CO<sub>2</sub> separation. This scheme outperforms other two routes in

terms of carbon atom efficiency (56.2%) and methane-to-methanol conversion efficiency. However, due to the external hydrogen input, Route III's exergy efficiency (70.8%) remains slightly lower than Route II's (71.2%). Moreover, in addition to the extra hydrogen cost, the higher methanol production rate increases the load on downstream separation processes, which consume more heat and steam compared to the other two routes. This results in a relatively lower low-pressure steam surplus (0.82 kg steam per kg MeOH). From a system integration perspective, the hydrogen supplementation path demonstrates significant advantages in methanol production capacity and resource utilization efficiency. However, its feasibility is highly dependent on the availability and economic viability of green hydrogen, which will be addressed in the subsequent techno-economic analysis.

The total electricity consumption of Route II is slightly lower than that of Route I, and the most significant difference between the two routes lies in the syngas compression unit, where compression power of Route II is 345.2 kW, a reduction of approximately 5% compared to Route I's 363.0 kW. This improvement is due to the reduced volume of syngas entering the methanol reactor after CO<sub>2</sub> separation, thereby reducing the compression power load. Additionally, with the same purge gas ratio, Route II's lower recycle gas ratio (3.52 vs. 3.91) results in lower electrical consumption for the recycle gas compressor (20.5 kW vs. 24.0 kW). In terms of specific electrical consumption per unit of methanol produced (0.438 kW·h per kg MeOH), Route II shows the best electrical energy efficiency. In contrast, Route III eliminates the need for CO<sub>2</sub> separation, thus saving electrical consumption for the MDEA circulation pump and regeneration tower. However, the addition of hydrogen results in an increase in the syngas feed gas volume. The high recycle ratio (3.95) in Route III leads to greater electrical power consumption for syngas and recycle gas compressors. As a result, Route III has the highest total electrical power consumption of the three configurations (675 kW), but its unit power consumption (0.448 kW·h per kg of MeOH) is still slightly lower than that of Route I. Although there

are differences in electrical consumption for auxiliary equipment (such as water pumps and air fans) among the three models, the overall differences are trivial, and these devices contribute relatively little to the total electrical consumption. The primary differences in electrical consumption still stem from power load biogas and syngas compressors.

### 3.2. Economic viability

We use minimum selling price (MSP) as the primary metric to compare the economic feasibility of three processing routes. The MSP represents the lowest price at which methanol must be sold to recover all capital and operational costs over the project lifetime, assuming no external subsidies or policy incentives [42–44]. The total capital expenditure (CAPEX) considered in this study includes all major equipment required, including an tubular reformer, methanol synthesis reactor, a CO<sub>2</sub> scrubbing tower based on MDEA absorption, crude methanol distillation columns, pumps, compressors, and heat exchangers. Regarding operational expenses, the estimation also accounts for catalyst maintenance. For the methanol synthesis catalyst (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>), a replacement cycle of 3 years is assumed, consistent with industrial standards for low-pressure methanol processes [45]. Importantly, the annual operating costs explicitly include the prorated expenses for periodic catalyst replacement over the 20-year plant lifespan, rather than only the initial charge, thereby providing a transparent and realistic long-term economic assessment.

Fig. 5 shows the techno-economic performance of three green methanol production pathways across a range of plant capacities, from 10 to 100 kilotonnes per year. For these calculations, an annual operating time of 8000 h is assumed, representing a typical availability factor for continuous industrial chemical plants to account for scheduled maintenance and unplanned shutdowns. Our computational framework determines the minimum selling price (MSP) of methanol required to ensure a positive net present value (NPV) over the plant lifetime and quantifies the corresponding capital expenditure (CAPEX) for each configuration as a function of production scale. For all the three processing routes, MSP decreases

as the plant scale increases, indicating substantial economies of scale. Among the three configurations, the post-reforming CO<sub>2</sub> removal strategy (Route II) consistently achieves the lowest MSP across all capacity ranges, reaching as low as 419 USD·t<sup>-1</sup> at 100 kt·a<sup>-1</sup>—well below the typical market benchmark for green methanol (600 USD·t<sup>-1</sup>). Notably, at a production scale of 10 kt·a<sup>-1</sup>, the post-reforming CO<sub>2</sub> removal pathway achieves an MSP of exactly 600 USD·t<sup>-1</sup>. In comparison, the pre-reforming CO<sub>2</sub> removal pathway (Route I) exhibits a similar declining trend but results in MSP that are consistently 30–50 USD·t<sup>-1</sup> higher than the post-reforming model. The green hydrogen supplementation pathway (Route III) yields the highest MSP across all scales, mainly due to the high cost of renewable hydrogen, assumed to be 3.0 USD·kg<sup>-1</sup> in this study. This price represents the comprehensive levelized cost of hydrogen (LCOH), which accounts for both the amortized capital expenditure (CAPEX) of the electrolyzer system and the levelized cost of renewable electricity. Based on the techno-economic assumptions derived from literature [46], electricity costs contribute approximately 70% to this LCOH, while the remaining 30% is attributed to the annualized CAPEX and fixed operating expenses of the electrolysis plant. This breakdown suggests that while electrolyzer cost reductions will improve the viability of Route III, its economic competitiveness remains primarily sensitive to the availability of low-cost renewable power. According to our sensitivity analysis, if the green hydrogen price drops to 1.85 USD·kg<sup>-1</sup>, the Route III will become the most economically viable option with the lowest MSP.

From a CAPEX perspective, the differences among pathways are minimal at small scales (<20 kt·a<sup>-1</sup>). However, as capacity increases, the green hydrogen supplementation pathway becomes the least capital-intensive, followed by the post-reforming CO<sub>2</sub> removal configuration, while the pre-reforming CO<sub>2</sub> removal route consistently shows the highest capital investment requirements. The relatively lower CAPEX of Route III can be attributed to two key design features: the elimination of the CO<sub>2</sub> scrubbing column in the syngas upgrading section reduces capital costs associated with gas purification; the integration of substantial green hydrogen into the methanol synthesis loop

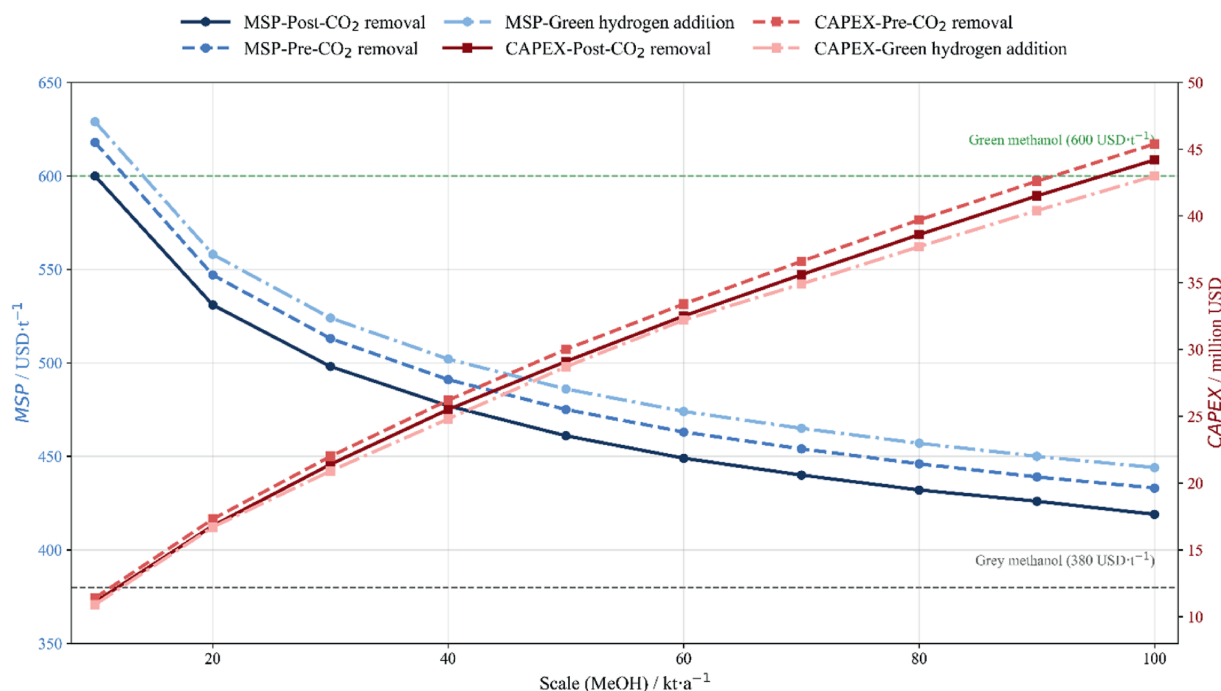


Fig. 5. Capital expenditure (CAPEX) and minimum selling price (MSP) of MeOH.

significantly enhances the methanol yield per unit of biogas input. Although this increases the MSP due to hydrogen cost, it reduces the specific capital cost per tonne of methanol produced by lowering the size of synthesis and downstream units.

Notably, the post-reforming CO<sub>2</sub> removal pathway (Route II) consistently achieves the lowest MSP across all scenarios. As shown in Table 1, this advantage arises primarily from lower biogas consumption and reduced overall energy demand, including lower electricity consumption and enhanced low-pressure (LP) steam recovery. Specifically, by removing CO<sub>2</sub> after the reformer, a greater portion of CO<sub>2</sub> from the feedstock is converted via reforming, allowing the system to meet methane conversion targets with less biogas and lower steam-to-carbon ratios. Additionally, this configuration enables methanol synthesis to operate at a lower recycle ratio, thereby reducing the size and power demand of compressors and circulators. These integrated benefits collectively result in the lowest MSP reported in this study—419 USD·t<sup>-1</sup> at 100 kt·a<sup>-1</sup>—making the post-reforming configuration highly competitive for large-scale implementation.

Benchmark cost comparisons further validate these findings. With reference prices of 380 USD·t<sup>-1</sup> for gray methanol and 600 USD·t<sup>-1</sup> for green methanol, only the post-reforming CO<sub>2</sub> removal pathway approaches cost parity with fossil-derived methanol at large scale. Moreover, this pathway achieves this performance with intermediate CAPEX levels, confirming it as the most promising configuration under the current techno-economic assumptions.

### 3.3. Environmental benefits

To evaluate the environmental impacts of three green methanol production routes, we conduct a cradle-to-gate life cycle assessment (LCA), using greenhouse gas (GHG) emissions as the primary indicator. Emissions are reported as the carbon dioxide equivalent per tonne of methanol produced (kg·t<sup>-1</sup>). Fig. 6 presents the comparative results for three biogas-based pathways, along with the conventional natural gas-to-methanol (NG-to-MeOH) pathway for baseline comparison. Each stacked bar in Fig. 6 is categorized into three parts: (i) Process Impact (gray), representing the total GHG emissions from energy and material consumption; (ii) CO<sub>2</sub> Avoided (blue), representing the carbon reduction benefits from biogenic carbon utilization or fossil resource displacement; and (iii) Net Emissions (red), calculated by subtracting avoided emissions from process impact.

Among the biogas-based pathways, Route II achieves the lowest net emissions across all scales, with 144 kg·t<sup>-1</sup> MeOH, followed by Route I (176 kg·t<sup>-1</sup>) and Route III (191 kg·t<sup>-1</sup>). The superior performance of Route II is mainly attributed to its lower electricity consumption, and steam balance simulations confirm that it leads to an increased production of low-pressure (LP) steam. This LP steam, when integrated into external heat recovery systems, contributes to additional carbon reduction benefits. Specifically, the life

cycle assessment employs a system-expansion (substitution) approach [47] to handle this co-product. The exported surplus LP steam is assumed to displace an equivalent amount of low-pressure steam produced in a conventional natural gas-fired industrial boiler (emission factor 0.33 kg·kg<sup>-1</sup>, consistent with Table S5), thereby generating avoided GHG emission credits. In contrast, Route III generates the highest greenhouse gas emissions. Although Route III boasts the highest carbon efficiency (56.2%) by fully utilizing biogenic carbon without physical separation, the integration of external hydrogen substantially increases the total volumetric flow and the recycle ratio in the synthesis loop (3.95, see Table 1). As detailed in our energy balance (Table 1), this results in the highest electrical power demand for gas compression (675 kW total). Under the assumed grid electricity emission factor, the indirect (Scope 2) emissions associated with this elevated compression work outweigh the benefits of higher carbon retention, ultimately leading to higher net GHG emissions compared to the other configurations. Although it shows a mid-level direct process impact, its lower LP steam production per unit of methanol results in the lowest CO<sub>2</sub> avoided among the three routes.

In contrast, the conventional NG-to-MeOH (Methanol production from natural gas) pathway exhibited the highest net GHG emissions (607 kg·t<sup>-1</sup>) [48], as it lacks any renewable carbon content or offset mechanism. However, even the least favorable biogas configuration (Route III) reduced net emissions by approximately 69% compared to the fossil-based process, highlighting the strong decarbonization potential of biogas-derived methanol. This LCA was conducted based on a functional unit of 1 tonne of methanol, with system boundaries including upstream biogas production, electricity usage, and CO<sub>2</sub> purification for Route I and II. The carbon credit calculations assume that all methane in biogas is of biogenic origin. To enhance transparency, the electricity emission factor used throughout the LCA is 0.45 kg·(kW·h)<sup>-1</sup> (TRACI 2.0, 100-year horizon, representing a Rest of World average mixed grid scenario sourced from the Ecoinvent database [49]). For Route III, green hydrogen is treated as a purchased input with net-zero upstream GHG emissions (consistent with its “green” designation and the absence of a separate emission factor in Table S5). Consequently, the electricity consumption reported for Route III reflects solely the on-site operational power demand within the plant battery limits (compressors, pumps, fans, etc.), with no double-counting of the electricity consumed by upstream electrolyzers. Detailed inventory data and emission factors can be found in the Supplementary Material.

### 3.4. Sensitivity analysis

To evaluate the impact of key physical or economic parameters on system feasibility, we conducted a sensitivity analysis to investigate the variation in the MSP of methanol under different electricity and biogas price scenarios. Based on the TEA and LCA results discussed above, we identified that among the three production pathways for green methanol, the post-reforming CO<sub>2</sub> removal process, when maintained at a large production scale (100,000 tonnes of methanol per year), demonstrates the optimal economic and environmental performance. Therefore, we selected route II for sensitivity analysis of two key economic parameters (see Fig. 7). In the figure, the x-axis represents electricity price (USD·(MW·h)<sup>-1</sup>), and the y-axis represents biogas price (USD·m<sup>-3</sup>). The heatmap color gradient reflects the MSP of methanol. The analysis reveals the impact of electricity price and biogas price fluctuations on the economics of green methanol production. In Fig. 7, biogas price has a significant impact on the production cost of green methanol. When electricity price remains constant, as the biogas price increases, MSP increases significantly. When the biogas price approaches 0.5 USD·m<sup>-3</sup>, the MSP of

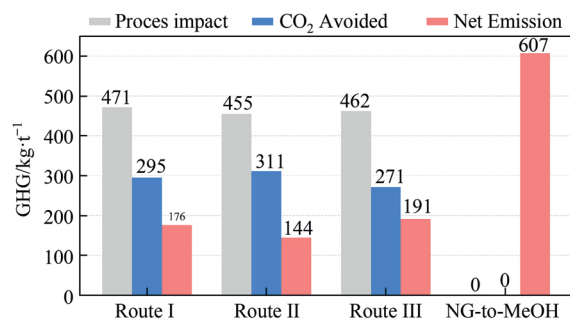


Fig. 6. Carbon emissions of three processing routes and NG-to-MeOH process.

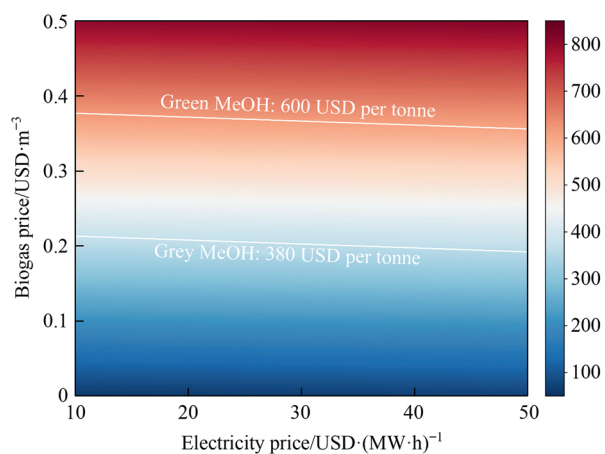


Fig. 7. MSP of MeOH as a function of electricity price and biogas price.

methanol reaches approximately  $800 \text{ USD} \cdot \text{t}^{-1}$ . This demonstrates the impact of biogas price fluctuations on production costs, especially in scenarios with higher biogas prices, where production costs rise sharply. In contrast, the impact of electricity price fluctuations on MSP is relatively small; under the same biogas price conditions, as electricity price increases, the MSP of methanol rises by only a small amount.

Further analysis suggests that, assuming a lower industrial electricity price, for MSP to reach the market price for green methanol ( $600 \text{ USD} \cdot \text{t}^{-1}$ ), the biogas price would need to be approximately  $0.36 \text{ USD} \cdot \text{m}^{-3}$ . This price is much higher than the assumed biogas price of  $0.23 \text{ USD} \cdot \text{m}^{-3}$  in industrial operations, indicating that, even under typical industrial electricity rates, the green methanol production project still has considerable profitability potential.

The sensitivity analysis results further demonstrate that MSP is not very sensitive to fluctuations in electricity prices, highlighting the significant advantage of biogas-based green methanol production in this study. Due to the system's efficient energy recovery and relatively low electricity consumption, the impact of electricity price fluctuations on MSP is minimal (electricity costs account for about 8% of the operating costs in green methanol production). Therefore, the project's profitability largely depends on the biogas price, with fluctuations in biogas price having a more pronounced effect on the project's economics, especially in markets with volatile prices.

The reduction in biogas price, particularly through policy subsidies, can significantly enhance the economic feasibility of green methanol production. Government incentives for biogas production from biomass resources (such as anaerobic digestion of poultry and livestock manure) can effectively reduce biogas costs [50], thereby lowering green methanol production costs and increasing profitability. Sensitivity analysis and TEA data indicate that a reduction in biogas prices significantly impacts production costs. For example, when the biogas price decreases from  $0.23 \text{ USD} \cdot \text{m}^{-3}$  to  $0.15 \text{ USD} \cdot \text{m}^{-3}$ , the production cost of green methanol can be reduced by approximately 28%. If the biogas price continues to decrease, the project's profitability potential increases exponentially. Furthermore, policy support helps stabilize market price fluctuations, mitigating the adverse effects of biogas price volatility on production costs, and further promotes the sustainable development of biogas-based green methanol production.

### 3.5. Future research directions

Based on the findings of this study, future research should address three areas to enhance the economic viability and

practical applicability of biogas-to-methanol processes: First, the diverse sources of biogas lead to significant variations in feed composition, especially in the  $\text{CH}_4/\text{CO}_2$  ratio, which can strongly influence the performance of different stoichiometric adjustment strategies. Future work should expand the process simulation framework by building a comprehensive database of composition data from varied biogas sources along with their optimized process parameters. Based on this database, a process optimization framework could be developed to reveal the optimal process design.

Second, sensitivity analysis indicates that fluctuations in biogas price have a dominant influence on methanol production cost. Therefore, future research should explore strategies to reduce the overall cost of biogas supply. Potential approaches include integrating biogas resources regionally, optimizing feedstock collection and transportation logistics, and designing cost-effective biogas supply chains. These efforts are essential to facilitate the large-scale deployment of biogas-based methanol production.

## 4. Conclusions

This study compares three processing routes for biogas-to-methanol conversion and evaluates their techno-economic and environmental performance. The results show that the downstream  $\text{CO}_2$  removal configuration (Route II) consistently shows the best economic performance, with the lowest minimum selling price (MSP) of  $419 \text{ USD} \cdot \text{t}^{-1}$  for a  $100 \text{ kt} \cdot \text{a}^{-1}$  plant. This advantage is mainly due to higher carbon utilization and improved energy efficiency. While the hydrogen supplementation configuration (Route III) achieves the highest methanol production, it results in a higher MSP due to the high cost of green hydrogen, indicating its potential for higher production but less favorable economics. Overall, this study recommends Route III as the most technically promising option in regions with abundant green hydrogen and policy support, while Route II is the most economically competitive configuration. Finally, it should be noted that this study is based on the assumption of steady-state operation, which serves as a necessary foundation for this comparative assessment. Future research could further expand this framework by incorporating dynamic scheduling considerations to account for the inherent intermittency of renewable hydrogen supply and the fluctuating availability of biogas. Addressing these dynamic operational challenges will be essential for optimizing the integration of biogas-to-methanol plants into future flexible energy grids.

## CRediT Authorship Contribution Statement

Xuebin Luan: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis. Zhiyu Jiao: Writing – original draft, Visualization, Validation, Software, Investigation, Formal analysis. Yufei Wang: Writing – original draft, Visualization, Software, Investigation, Formal analysis, Conceptualization. Congcong Niu: Writing – original draft, Validation, Methodology, Investigation, Formal analysis. Xuandong Liu: Visualization, Software, Methodology, Formal analysis. Run Xu: Writing – original draft, Validation, Investigation, Formal analysis. Guofu Xia: Writing – original draft, Validation, Investigation, Formal analysis. Hongwei Li: Investigation, Formal analysis. Le Zhang: Writing – original draft, Validation, Supervision, Software, Investigation, Formal analysis, Data curation, Conceptualization. Jiase Ma: Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2026.03.029>.

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