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Sustainable Biomethanol and Biomethane Production via Anaerobic Digestion, Oxy-Fuel Gas Turbine and Amine Scrubbing CO₂ Capture

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Abstract: Energy policies around the world are increasingly highlighting the importance of hydrogen in the evolving energy landscape. In this regard, the use of hydrogen to produce biomethanol not only plays an essential role in the chemical industry but also holds great promise as an alternative fuel for global shipping. This study evaluates a system for generating biomethanol and biomethane based on anaerobic digestion, biogas upgrading, methanol synthesis unit, and high-temperature electrolysis. Thermal integration is implemented to enhance efficiency by linking the oxy-fuel gas turbine unit. The integrated system performance is evaluated through thermodynamic modeling, and Aspen Plus V12.1 is employed for the analysis. Our findings show that the primary power consumers are the Solid Oxide Electrolysis Cell (SOEC) and Methanol Synthesis Unit (MSU), with the SOEC system consuming 824 kW of power and the MSU consuming 129.5 kW of power, corresponding to a production scale of 23.2 kg/h of hydrogen and 269.54 kg/h of biomethanol, respectively. The overall energy efficiency is calculated at 58.09%, considering a production output of 188 kg/h of biomethane and 269 kg/h of biomethanol. The amount of carbon dioxide emitted per biofuel production is equal to 0.017, and the proposed system can be considered a low-carbon emission system. Key findings include significant enhancements in biomethanol capacity and energy efficiency with higher temperatures in the methanol reactor.

Keywords: biogas upgrading; methane production; methanol synthesis; thermodynamics; CO₂ utilization; carbon capture



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1. Introduction

The Energy Union strategy of the European Commission aims for net-zero greenhouse gas emissions by 2050 [1]. To achieve this, there is a growing reliance on renewable energy sources (RES) like wind and solar, which generate power intermittently, depending on factors like weather and sunlight [2,3]. To stabilize energy output and expand renewable energy use, energy storage solutions are crucial. One method is converting energy from renewables into hydrogen through electrolysis, which can then be used to produce biofuels [4,5]. This study explores a methanol production system utilizing high-temperature electrolysis and anaerobic digestion.

In previous studies, it has been established that the specific energy consumption of Solid Oxide Electrolysis Cells (SOECs) is lower than that of alkaline and proton exchange membranes (PEMs) electrolyzers [6]. Significant research efforts have focused on the utilization of high-temperature electrolysis cells. AlZahrani and Dincer (2018) [7] conducted a modeling and performance optimization study on a 1 MW Solid Oxide Electrolysis Cell (SOEC) system for hydrogen production. Their study revealed that the SOEC system could achieve a second-law efficiency of 87.12% under optimal conditions, with a stack temperature of 1168 K, a pressure of 8 MPa, and a current density of 5000 A/m². Daneshpour and Mehrpooya (2018) [8] combined a photovoltaic solar thermal collector with a Solid Oxide

Electrolysis Cell featuring planar cathodes to generate both hydrogen and power. Their experimental validation showed that the system operated effectively under exothermic conditions, eliminating the need for an additional heater. This setup achieved an efficiency of 54%, resulting in the production of 7458 kg/h of hydrogen. Schiller et al. (2019) [9] established an experimental arrangement utilizing Solid Oxide Electrolysis Cells to produce hydrogen. Their configuration required 1.65 kW of electricity to power the SOEC stack, producing 1600 L of hydrogen over a 4-h period. Thermodynamically, the inclusion of a high-temperature source was vital to reducing power consumption and enhancing system efficiency. As a result, the system employed a solar source for high-temperature steam generation, incorporating a solar simulator, accumulator, SOEC stack, and steam generator. This configuration produced 5 kg/h of steam, with 10% hydrogen recycled from the output. This mixture was then supplied to a SOEC unit with 12 cells. Researchers determined that the system could attain significant energy efficiency under certain conditions, including a current density of 1.25 A/m^2 , a steam temperature of 775°C , and a steam conversion efficiency of 70%. Both experimental and theoretical investigations underscore the advantages of high-temperature electrolysis cells compared to their low-temperature counterparts. These high-temperature cells utilize exothermic reactions to minimize the requirement for additional heat in the SOEC process and incorporate a hydrogen-steam blend in the SOEC input.

Recent research has increasingly focused on converting green hydrogen into methanol due to the high versatility and utility of biomethanol as a fuel. Many studies strive to improve the performance of methanol synthesis. Leonzio et al. (2019) [10] conducted a study comparing three different methanol reactors under equilibrium conditions: a single-channel reactor, a reactor with gas recycling and water condensation, and a membrane reactor with water filtration. The findings showed that the reactor with gas recycling and water condensation achieved the highest CO_2 to methanol conversion efficiency, reaching 69%. This optimal conversion was achieved at a temperature of 473 K and a pressure of 55 bar.

Numerous studies have explored integrating methanol production with electrolysis cells. In a study conducted by Parigi et al. (2019) [11], the authors investigated the production of synthetic fuels, focusing on methane and methanol, through two different methods involving high-temperature water splitting using Solid Oxide Electrolysis Cells. Their results indicated that power-to-methanol and power-to-methane processes could reach efficiencies of 59% and 77%, respectively. Furthermore, in Tinoco et al. (2016) [12], a comparison was made between Solid Oxide Electrolysis Cells (SOEC) and proton exchange membrane (PEM) electrolyzers to produce methanol, with a focus on their economic aspects. The analysis showed that while SOECs involve higher initial investment costs, PEM electrolyzers have greater operating and maintenance expenses. Thus, constructing SOEC systems within a shorter time frame is advisable to minimize these costs. Additionally, it was found that the production cost of methanol using both SOEC and PEM electrolyzers was significantly higher than the market price, at 15 and 2.5 times more, respectively. This indicates a need for substantial improvements in electrolysis technology to make these systems economically viable. Moreover, Lonis et al. (2019) [13] explored a combined system for methanol production utilizing hydrogen produced by SOECs. Their strategy incorporated thermal energy storage (TES) and thermal integration techniques to redirect surplus heat from a fuel cell to both the SOEC and the methanol synthesis unit (MSU). This incorporation of TES improved the overall efficiency from 27.58% to 32.93%. Moreover, Zhang and Desideri (2020) [14] optimized a power-to-methanol system that utilizes co-electrolysis of CO_2 and H_2O with SOEC. Their approach involved introducing steam, CO_2 , and some hydrogen into the cathode, achieving an energy efficiency of 72%. Nevertheless, the system was found to be economically unviable, mainly because of the high cost of the SOEC stack, its relatively short operational lifespan, and the elevated cost of power. Additionally, Ostadi et al. (2023) [15] examined various approaches to enhance methanol production by utilizing hydrogen obtained from diverse sources, such as water

electrolysis, natural gas pyrolysis, or a combination of both. Integrating hydrogen into the methanol production process nearly doubled the carbon conversion efficiency from 44% to 94%. It should be noted that this study required significant fossil fuel consumption during the natural gas pyrolysis process and the use of electricity in the air separation unit, resulting in some carbon dioxide emissions into the environment. As an additional improvement, utilizing waste heat from the biomethanol synthesis unit could potentially reduce environmental impacts.

It should be noted that power-to-methanol processes are efficient when integrated with biogas plants [16]. In this regard, Eggemann et al. (2020) [17] evaluated the environmental sustainability, covering the entire life cycle up to the production gate, of an innovative power-to-fuel system designed for the synthesis of methanol. In their system, the surplus carbon dioxide generated during biogas production was harnessed for methanol synthesis, while hydrogen was generated through electrolysis powered by wind energy. In all scenarios examined, substantial environmental improvements are evident compared to conventional methanol production from fossil resources, particularly in the areas of acidification and eutrophication. Their plant was economically competitive compared to fossil-based alternatives. Riaz et al. (2022) [18] developed a system to produce biomethanol by separating carbon dioxide from biogas using membranes and producing hydrogen through plasma electrolysis. This method resulted in a 15.7% efficiency improvement for the methanol synthesis unit compared to the baseline. A detailed exergy analysis of the process identified losses in heaters, separators, and reactors. Integrating heat afterward led to a 6.6% in energy savings. Hai et al. (2023) [19] introduced an innovative approach to producing methanol with water electrolysis and biogas upgrading by water condensation subsystems. In the context of exergy analysis, the CO₂ capture and gas turbine cycle were responsible for an 80% share of exergy destruction, mainly due to a combustion chamber. In addition, the production cost of methanol was found to be 0.124 \$/kg. Additionally, Gray et al. (2022) [20] examined the energy equilibrium associated with the production of biomethanol when combined with a biogas plant that co-digests grass silage and dairy slurry. They observed that the integration of power-to-methanol with the biogas system resulted in a 50% increase in gross energy production. It should be noted that the electrolysis cell represented the highest demand, consuming 74% of the total electricity.

Considering the research gaps identified in the existing literature, this study seeks to improve current systems with regard to biomethanol and biomethane production and energy efficiency. The integrated system introduced in this investigation has not previously been modeled or assessed, and its main innovations can be summarized as follows.

In our study, we have utilized data related to anaerobic biogas production that is directly comparable to the work of Mir Masoumi et al. (2018) [21], specifically focusing on a full-scale industrial anaerobic digestion plant located in Tabriz, Iran. The municipal sewage sludge used as feedstock in this plant has a mass flow rate of approximately 8.608 kg/s, forming the basis of our system's design and modeling, ensuring our results are grounded in real-world, industrial-scale operations. Still, we have extended this analysis by integrating additional subsystems, such as the biogas upgrading unit and methanol synthesis unit, to optimize the production of biomethane and biomethanol.

The integrated system introduced in this investigation introduces several novel elements, summarized as follows:

- It utilizes highly efficient Solid Oxide Electrolysis Cells (SOEC), outperforming low-temperature electrolysis cells.
- Oxygen produced by the SOEC is used in the gas turbine cycle, eliminating the need for an Air Separation Unit (ASU).

- The system integrates biogas upgrading methods (amine scrubbing), Solid Oxide Electrolysis Cells, and oxy-fuel gas turbines to capture CO₂ and convert hydrogen into biomethanol, addressing energy storage and safety concerns.
- Thermal integration with an oxy-biogas boiler generates steam for the SOEC, and detailed thermodynamic modeling and sensitivity analysis are conducted.

2. System Description

The system proposed in this study, depicted in Figure 1, integrates various processes to optimize energy usage and biofuel production. Key components include:

- Anaerobic digestion unit (ADU),
- Oxy-fuel gas turbine unit (OFGTU) integrated with carbon capture by water condensation techniques,
- High-temperature solid oxide electrolysis (SOEC),
- Biogas upgrading unit (BUU) by amine scrubbing process for carbon dioxide separation and from biogas,
- Methanol Synthesis Unit (MSU).

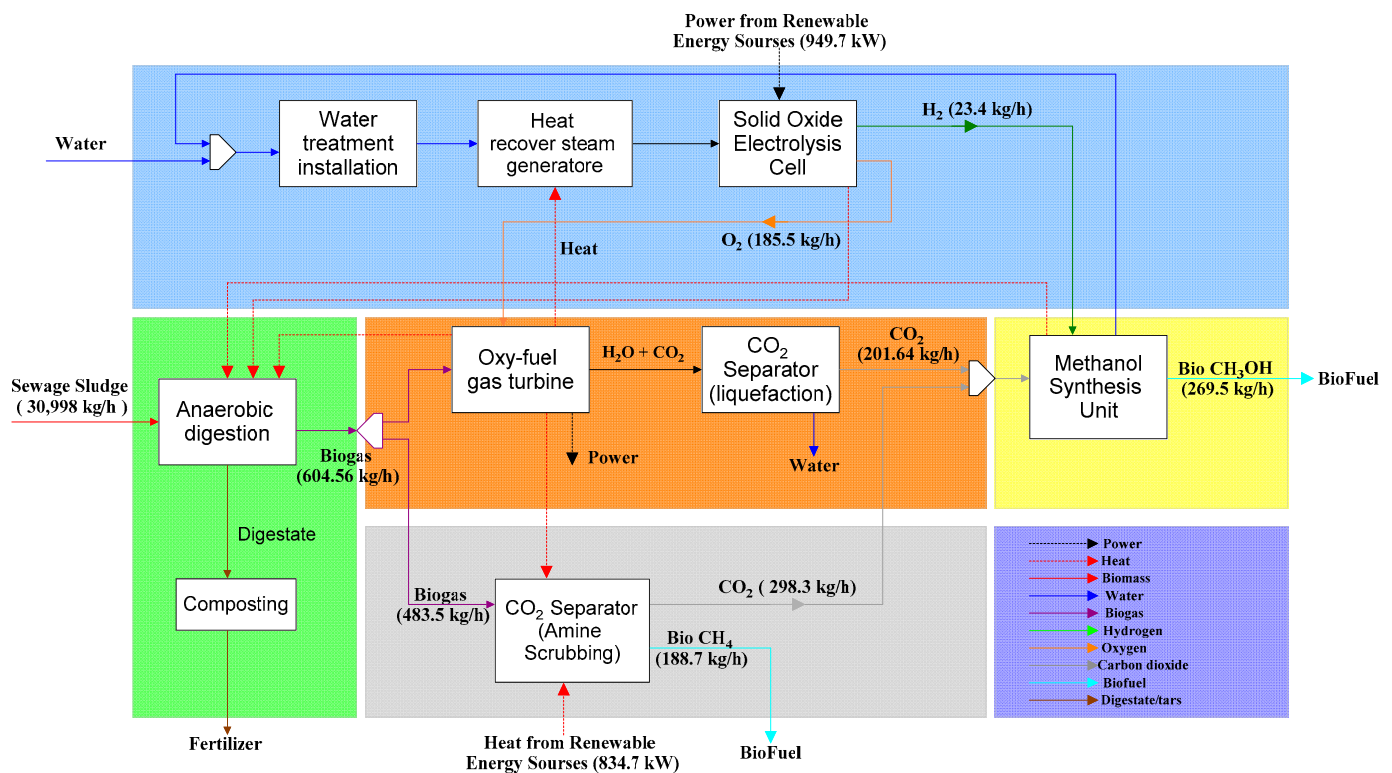


Figure 1. Simplified scheme of the proposed system to produce biofuels.

Sewage sludge serves as the primary feed material for the anaerobic digestion system. A portion of the biogas generated is sent to the oxy-fuel combustion system, which sources its oxygen from the high-temperature solid oxide electrolysis system. Meanwhile, another part of the biogas is diverted to the biogas upgrading system, where methane and carbon dioxide are produced. The carbon dioxide from the biogas upgrading system, oxy-fuel gas turbine system, and the hydrogen from the solid oxide electrolysis unit are then transferred to the methanol synthesis unit, facilitating methanol production in a more efficient manner.

2.1. Anaerobic Digestion Unit

As depicted in Figure 2, the anaerobic digestion subsystem process starts with the municipal sewage sludge as feedstock, which undergoes heat exchange and is pumped to elevate its temperature and pressure before entering the thermal pretreatment tank. The pretreatment tank, operating at 90 °C, has its heat demand satisfied by energy recovered from HX2, HX4 of the oxy-fuel gas turbine and O2-HX, H2-HX of the SOEC. This temperature is selected based on studies, including Mirmasoumi et al. [21], which demonstrated that thermal pretreatment at 90 °C for 0.5 h can significantly enhance the biodegradability of sewage sludge, leading to a 59.82% increase in biomethane productivity compared to non-treated sludge under mesophilic conditions. Additionally, the pretreatment process and the increase in digestion temperature to thermophilic conditions have been shown to boost biomethane productivity by up to 160.8%. This approach not only enhances biogas yield but also improves the overall efficiency and energy recovery of the anaerobic digestion process. The feedstock's pressure is increased to 3.5 bar to ensure efficient entry into the digesters. Biogas produced at 1.5 bar and 55 °C under thermophilic conditions is purified and dehumidified to remove hydrogen sulfide and water vapor, and this action causes its temperature to drop to 19 °C; subsequently, 20% of the biogas is directed to the oxy-fuel gas turbine unit, while the remaining portion enters the biogas upgrading unit. Table A1 of Appendix A provides the elemental analysis of the organic components in sewage sludge, while Table A2 of Appendix A presents the parameters and operating conditions for the thermophilic anaerobic digestion of the sewage sludge. These tables summarize the assumptions, inputs, and outputs used in our thermodynamic modeling. The technical data of the anaerobic digestion plant in Tabriz, including details such as the dry matter content of sludge, specific biogas yield, methane content, and operational temperatures, are comprehensively provided in these tables, ensuring that all relevant information is available for review.

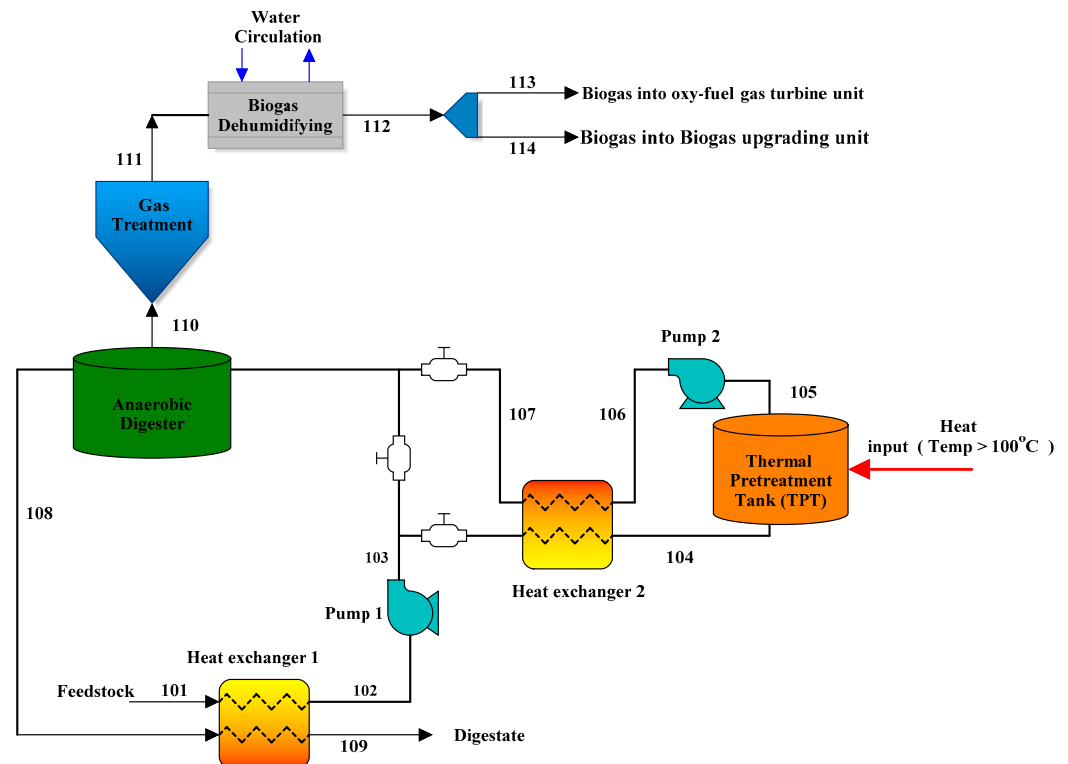


Figure 2. Schematic diagram of the anaerobic digestion unit.

2.2. Solid Oxide Electrolysis Cell Integrated with the Oxy-Fuel Gas Turbine Unit

The subsystem involving the Solid Oxide Electrolysis Cell (SOEC) and the oxy-fuel gas turbine, shown in Figure 3, represents an integrated energy conversion system aimed at efficiently producing hydrogen and capturing carbon dioxide. In the SOEC subsystem, water preheated in the heat recovery steam generator (HRSG) is combined with additional steam from the phase separator (SEP 2) before entering the SOEC stack. With extra heat and power, the water undergoes electrolysis, splitting into hydrogen and oxygen. The oxygen is then supplied to the oxy-fuel gas turbine, while the hydrogen is sent to the methanol synthesis unit for further processing.

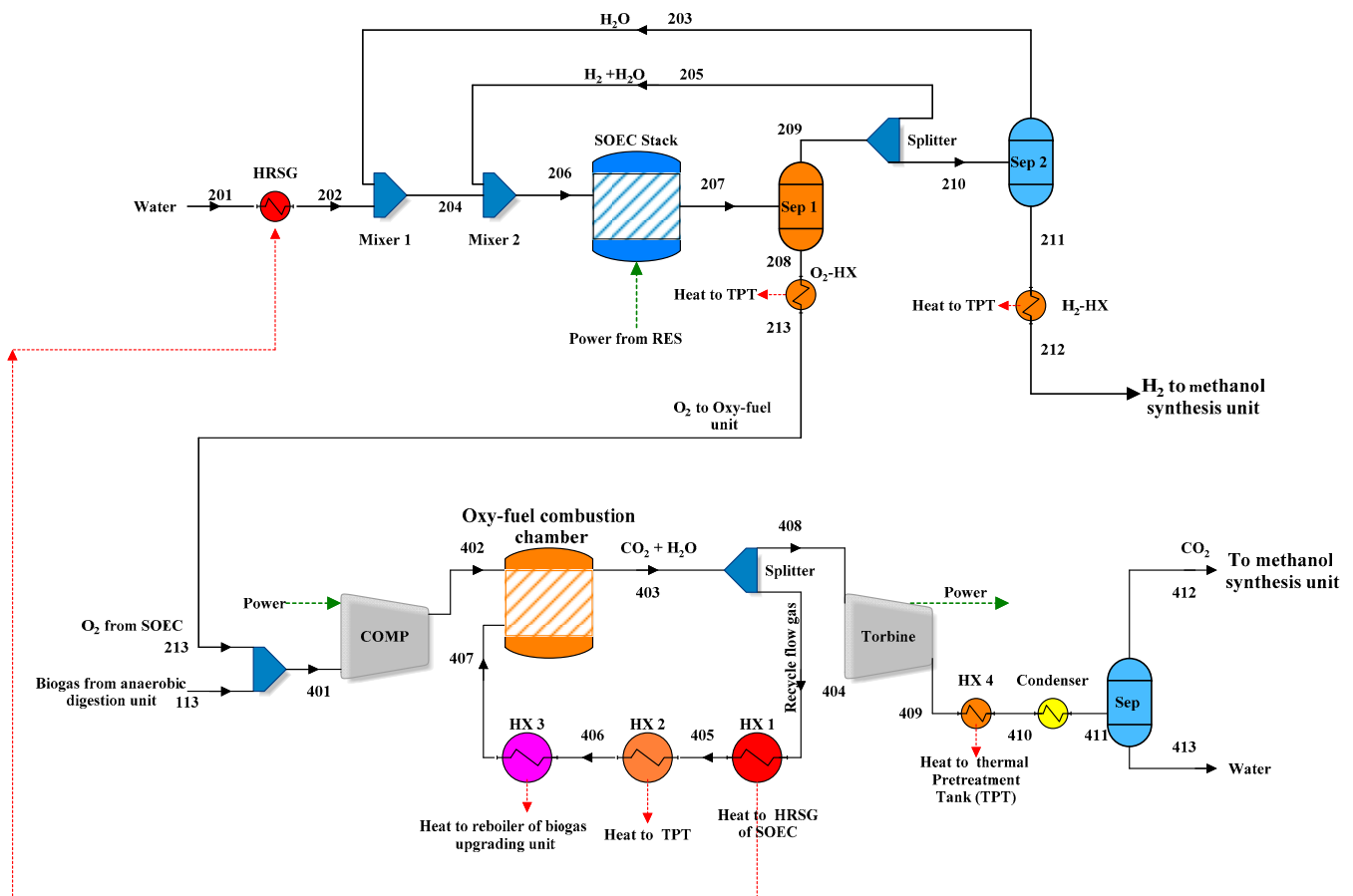


Figure 3. Schematic diagram of the Solid Oxide Electrolysis Cell (SOEC) integrated with the Oxy-fuel gas turbine unit.

In the oxy-fuel gas turbine subsystem, biogas from the anaerobic digestion process is compressed to increase its pressure before being mixed with oxygen from the SOEC in the combustion chamber. This reaction generates CO_2 and H_2O , which pass through heat exchangers (HX3, HX2, HX1), capturing thermal energy for various system components, including the thermal pretreatment tank (TPT), HRSG, and the biogas upgrading units reboiler. The turbine, located after the combustion chamber, converts the extracted thermal energy into electricity. After passing through the turbine, the water vapor is condensed in a phase separator to remove the water, and the CO_2 is sent to the methanol synthesis unit for conversion into methanol.

2.3. Biogas Upgrading and Utilization

Amine scrubbing is a method used to remove unwanted gases from a gas mixture by employing a liquid amine solution, which absorbs the target gas molecules. This absorption process is influenced by the solubility of the gas in the amine solution and its chemical affinity for the amine. The technique involves a sequence of chemical interactions between the amine and gases such as CO₂, resulting in the formation of new bonds. Various amines, such as MDEA, DEA, DGA, and MEA, are commonly utilized for this purpose. This method can produce high-purity methane (94–98%), but it requires significant heat to regenerate the amine solution [22]. Figure 4 illustrates the process layout modeled in Aspen Plus.

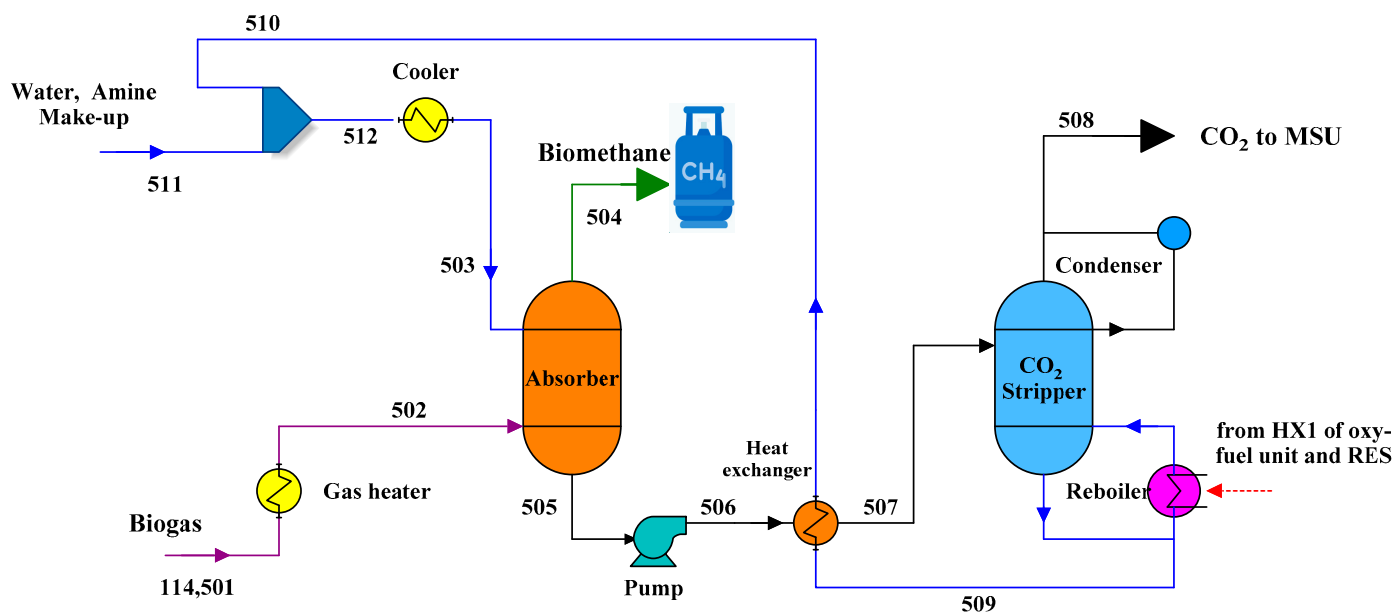


Figure 4. Schematic diagram of the biogas upgrading unit.

In the biogas upgrading system, depicted in Figure 4, the biogas stream (501) is initially heated to 33 °C in a heater (502) before moving to the absorber (503). The absorber operates under a slight overpressure of 1.05 bar and interacts with a 30% MEA solution introduced at 20 °C. In this environment, the MEA solution absorbs CO₂ and H₂S from the biogas as it moves down the absorber column.

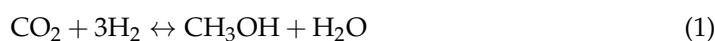
After the absorption phase, the MEA solution, now rich in absorbed gases, passes through a heat exchanger (506) to capture heat from the regenerated amine solution, which has been processed in the stripper (509) and heated to 80 °C. The regenerated MEA, now free of CO₂, preheats the incoming rich amine, enhancing energy efficiency. The separated CO₂ (508) is then sent to the methanol synthesis unit (MSU) for conversion into useful chemicals. To maintain solvent capacity for continuous operation, MEA make-up (511) is added to compensate for any losses during the gas treatment process.

2.4. Methanol Synthesis Unit

In the methanol synthesis subsystem, shown in Figure 5, three streams are combined to produce methanol through CO₂ hydrogenation. These streams consist of hydrogen from the Solid Oxide Electrolysis Cell, CO₂ from the biogas upgrading unit, and CO₂ from the oxy-fuel gas turbine. All streams are compressed and mixed using four-stage compressors. In addition, the streams are blended with recycled gases before being fed into the methanol reactor and its associated heater.

The gases exiting the reactor are used to transfer thermal energy to the methanol-water mixture, which is then fed into a distillation column. Following this, the gases are cooled and routed to the drum and flash separators to distinguish between the gas and liquid phases. At this point, the purity of the biomethanol reaches around 99.5%. The liquid is then directed to the distillation column for further purification, separating biomethanol and water.

In the methanol production plant, syngas serves as the primary raw material undergoing the reactions below [13]:



These reactions are exothermic and operate at lower temperatures to achieve maximum conversion efficiency, using a Cu/ZnO/Al₂O₃ catalyst temperature range of 210–280 °C. The Cu/ZnO/Al₂O₃ catalyst is preferred for methanol synthesis because of its high selectivity, stability, and performance. Additionally, the process needs to minimize the concentration of CO₂ in the syngas to prevent the reverse water-gas shift reaction (RWGS), which would otherwise increase the production of water and CO, as shown in reaction (3) [23].

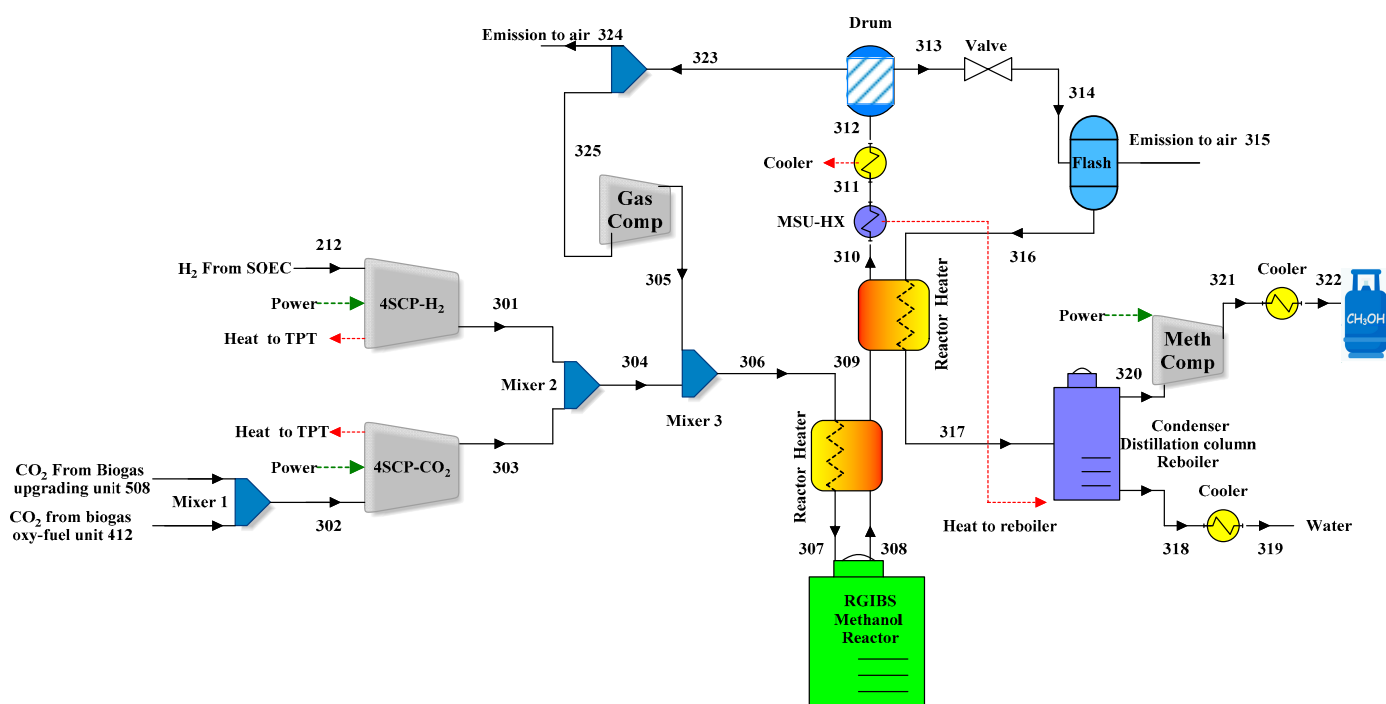


Figure 5. Schematic diagram of the methanol synthesis unit.

3. Materials and Methods

The entire proposed cycle was modeled and analyzed using Aspen Plus V12.1. Additional calculations were necessary for the SOEC stack within Aspen Plus, detailed in previous work [24]. The data required to simulate the whole proposed system are presented in Table 1 for the elemental composition of the organic component in the sewage sludge. Experimental data from Ref. [21] was used, as shown in Table A1 of Appendix A.

Table 1. Input data used to model the proposed system.

Parameter	Value	Ref.
Ambient temperature	25 °C	[25]
Ambient pressure	1 bar	[26]
Anaerobic digestion unit (ADU)		
Biomass type	Sewage sludge	[21]
Digestion type	Thermophilic	[21]
Outlet temperature of the digester	55 °C	[21]
Outlet temperature of the thermal pretreatment tank	90 °C	[21]
Temperature of the sewage sludge	18 °C	[21]
Mass flow rate of biomass	8.608 kg/s	[21]
Biogas production of anaerobic digestate	0.167933 kg/s	[21]
Biogas split fraction into the oxy-fuel gas turbine unit	20%	
Biogas split fraction into the biogas upgrading unit	80%	
LHV of biogas	20,198 kJ/kg	[21]
LHV of hydrogen	119,950 kJ/kg	[27]
LHV of methanol	19,920 kJ/kg	[27]
LHV of methane	50,020 kJ/kg	[27]
Biogas upgrading unit (BUU)		
Pressure of absorber and Stripper	1.05 and 1.5 bar	[22]
Number of stages in absorber and stripper	10 and 10	[22]
Diameter of absorber and Stripper	0.37 and 0.725 m	[22]
Height of absorber and Stripper	3.5 and 4.8 m	[22]
Packing dimension of absorber and stripper	38 and 50 mm	[22]
Calculation method	ELECNRTL-NRTL	[22]
Solid Oxide Electrolysis Cell (SOEC)		
Split fractions of stream	10% and 90%	[13]
Stack temperature	750 °C	[8]
Outlet temperature of H ₂ , O ₂	100 °C	[8]
Faraday's constant, F	96,487 °C/mol	[28]
Anode effective diffusion, D_a^{eff}	$2 \times 10^{-5} \text{ m}^2/\text{s}$	[29]
Cathode effective diffusion, D_c^{eff}	$5.11 \times 10^{-5} \text{ m}^2/\text{s}$	[29]
Anode activation energy, E_a^{act}	120,000 J/mol	[29]
Cathode activation energy, E_c^{act}	100,000 J/mol	[29]
Anode pre-exponential factor, γ_a	2.05 A/m ²	[30]
Cathode pre-exponential factor, γ_c	1.34 A/m ²	[30]
Anode thickness, δ_a	$1.75 \times 10^{-5} \text{ m}$	[29]
Cathode thickness, δ_c	$3.13 \times 10^{-4} \text{ m}$	[29]
Electrolyte thickness, δ_e	$1.25 \times 10^{-5} \text{ m}$	[29]
Ideal gases constant, R	8.314 J/mol/K	[29]
Current density, J	10,000 A/m ²	[31]
Cell active area, A_{cell}	0.324 m ²	[8]

Table 1. Cont.

Parameter	Value	Ref.
Methanol Synthesis Unit (MSU)		
Pressure of gases entering the MSU	51 bars	[32]
Outlet temperature of the coolers between 4SCP of H ₂ and FG	157 °C	[33]
Outlet temperature of the coolers between 4SCP of CO ₂	125.6 °C	[33]
Pressure drops in heat exchangers in the MSU	1 bar	[33]
Inlet and outlet temperature of the methanol reactor	210 and 280 °C	[32]
Inlet temperature of the distillation column	80 °C	[33]
Inlet temperature of drum	35 °C	[33]
Outlet temperature and pressure of the valve	32 °C and 1.2 bar	[33]
Number of stages in the distillation column	20	[32]
Pressure of the partial condenser and reboiler	1 bar	[33]
Temperature of methanol and water leaving their coolers	40 °C	[33]
Outlet pressure of the methanol compressor	1.2 bar	[33]
Isentropic efficiency of the methanol and gas compressors	0.85	[34]
Separate fraction of exhaust gases from stream 324	1.01%	[33]
Oxy-fuel gas turbine unit		
Pressure of the combustion chamber	6 bars	[1]
Split fraction of exhausted gas into recycled flue gas	85%	[1]
Temperature of recycled flue gas into the combustion chamber	300 °C	[33]
Pressure of the condenser	1 bar	[33]
Temperature of the condenser	35 °C	[33]

The total energy efficiency of the system is expressed in Equation (4). This parameter represents the ratio of the total output gains of the proposed system, which included biomethane and biomethanol to the energy inputs, which include biogas produced from the anaerobic digestion system as well as power and heat sourced from renewable systems [35–37]:

$$\eta_{en} = \frac{(\dot{m} \cdot LHV)_{CH_3OH} + (\dot{m} \cdot LHV)_{CH_4}}{(\dot{m} \cdot LHV)_{Biogas} + (\dot{W}_{in} - \dot{W}_{out})/\eta_w + (\dot{Q}_{REB,BUU} - Q_{HX3,OFGTU})} \quad (4)$$

$$\dot{W}_{out} = \dot{W}_{Tur,OFGTU} \quad (5)$$

$$\dot{W}_{in} = \dot{W}_{CP,OFGTU} + \dot{W}_{SOEC} + \dot{W}_{MethCP,MSU} + \dot{W}_{GasCP,MSU} + \dot{W}_{4SCP,H_2,MSU} + \dot{W}_{4SCP,O_2,MSU} + \dot{W}_{pump1,ADU} + \dot{W}_{pump2,ADU} + \dot{W}_{pump,BUU} \quad (6)$$

In these equations, $(\dot{m} \cdot LHV)_{CH_3OH}$ and $(\dot{m} \cdot LHV)_{CH_4}$ refer to the chemical energy of biomethanol and biomethane production in the methanol syntheses unit and biogas upgrading unit, respectively. Additionally, $\dot{W}_{out}$ and $\dot{W}_{in}$ are the net of production and electricity consumption, respectively. η_w is equal to 1/3 reported in Ref [38]. The $\dot{Q}_{REB,BUU}$ and $Q_{HX3,OFCU}$ present the reboiler duty in the stripper column of the biogas upgrading unit and heat duty of heat exchanger 3 in the oxy-fuel gas turbine unit, respectively. The subscripts Meth, CP, and 4SCP refer to the methanol compressor and four-stage compressor, respectively.

Emitted CO₂ per biofuel production, E_{CO_2} , is the ratio of total kg of CO₂ emitted from the proposed system per kg of biofuel produced [15], as reported in Equation (7).

$$E_{\text{co2}} = \frac{\dot{m}_{\text{CO}_2}}{\dot{m}_{\text{bCH}_4} + \dot{m}_{\text{bCH}_3\text{OH}}} \quad (7)$$

4. Results and Discussion

4.1. Model Verification

The model developed for this study was validated using data from existing literature. The validation results of the methanol synthesis unit have been shown in the previous reference work [24]. Figure 6 demonstrates the validation of the SOEC stack model through comparison with the results from Ref. [30]. Table 2 verifies the results of the temperature, pressure, mass flow rate, and composition of important streams by comparing them with Ref. [22]. The results indicate a strong agreement between this study and the referenced works.

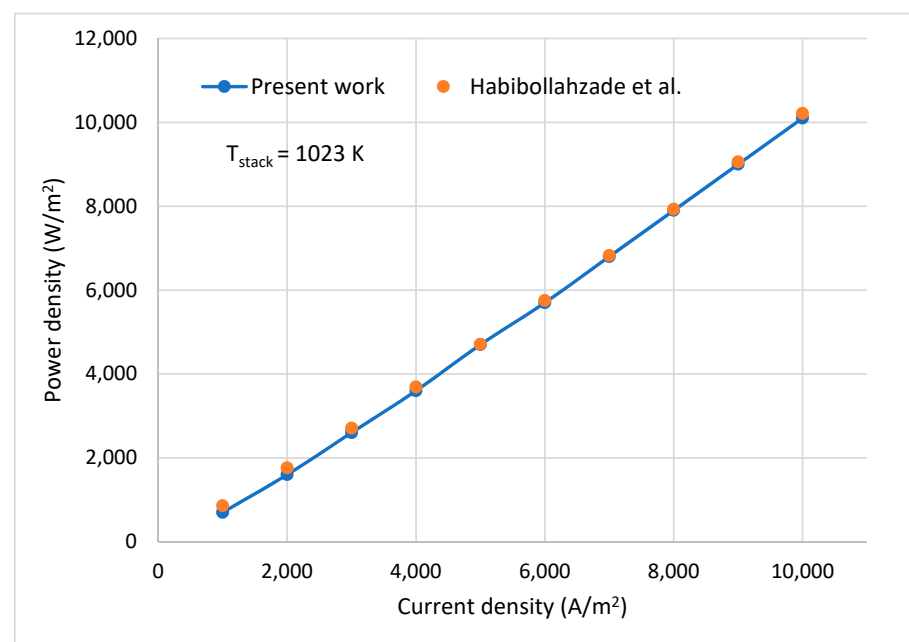


Figure 6. Comparison of the results of SOEC modeling between the present study and ref. [30].

Table 2. Comparison of the stream properties of the biogas upgrading unit between the present study and ref. [22].

	Ref.			Present Work			Mass Flow of Ref. [22]			Mass Flow of Present Work		
	T (°C)	P (bar)	$\dot{m}$ (kg/h)	T (°C)	P (bar)	$\dot{m}$ (kg/h)	$\dot{m}_{\text{CO}_2}$ (kg/h)	$\dot{m}_{\text{CH}_4}$ (kg/h)	$\dot{m}_{\text{H}_2\text{O}}$ (kg/h)	$\dot{m}_{\text{CO}_2}$ (kg/h)	$\dot{m}_{\text{CH}_4}$ (kg/h)	$\dot{m}_{\text{H}_2\text{O}}$ (kg/h)
Biogas inlet (201)	30	1.013	604.56	30	1.013	604.56	371.67	214.094	11.890	371.670	214.094	11.890
Produced CH ₄ (204)	20.094	1.013	229.12	20.012	1.013	225.83	0.102	216.883	5.365	0.004	214.056	4.860
Produced CO ₂ (208)	48.183	1.5	389.67	46.98	1.5	382.05	376.64	0.039	12.770	371.678	0.040	10.300

4.2. Basic Results

The thermodynamic properties of each state point in the proposed system for the subsystems are outlined in Tables A3–A7 of Appendix A for all subsystems modeled in Aspen Plus software. State numbers in these tables match Figures 1–5. It should be noted that in Table A3 of Appendix A, water properties have been used to simulate the sewage sludge as biomass in the anaerobic digestion system since more than 95% of the sewage sludge content is water [39]. It is also worth noting that Table A4 of Appendix A is associated with the SOEC system, Table A5 of Appendix A with the MSU, Table A6

of Appendix A with the oxy-fuel gas turbine unit, and Table A7 of Appendix A with the biogas upgrading process.

Table 3 provides the key performance metrics of the biofuel production system, indicating an overall energy efficiency of 58.09%. The system's output includes the production of 188.68 kg/h of biomethane and 269.54 kg/h of biomethanol. The biofuel production process requires significant electricity consumption of 949.7 kW and heat consumption of 839.38 kW. The heat, used primarily in the reboiler of the biogas upgrading system, operates at approximately 115 °C and is derived from renewable energy sources.

Table 3. Overall results of the proposed system for biofuel generation.

Parameter	Unit	Value
Overall energy efficiency	%	58.09
Biomethane capacity of the overall system	kg/h	188.68
Biomethanol capacity of the overall system	kg/h	269.54
Heat consumption of the overall system	kW	839.38
Power consumption of the overall system	kW	949.7
Number of SOEC cells	-	3 × 80
Hydrogen yield of SOEC	kg/h	23.2
Oxygen yield of SOEC	kg/h	184.1
Heat consumption of the biogas upgrading unit	kW	−930
Heat consumption of the thermal pretreatment tank	kW	−500.77
Heat generation of the oxy-fuel unit into the biogas upgrading unit (HX3)	kW	90.612
CO ₂ capacity in the biogas upgrading unit	kg/h	298.3
CO ₂ capacity in the oxy-fuel gas turbine unit	kg/h	201.64
CO ₂ utilization in MSU	kg/h	499.95
CO ₂ emission from the whole system (stream 315,324 of MSU)	kg/h	7.98
Emitted CO ₂ per biofuel production, E_{CO_2}	-	0.01742

The solid oxide electrolyzer cell (SOEC) system, designed with three blocks containing 80 cells each, generates 23.2 kg/h of hydrogen and 184 kg/h of oxygen. The biogas upgrading system contributes an additional 188.68 kg/h of biomethane and 298.3 kg/h of CO₂. The methanol synthesis unit (MSU) utilizes 23.2 kg/h of hydrogen from the SOEC and 499.95 kg/h of CO₂, sourced from both the biogas upgrading process and the oxy-fuel gas turbine unit, to produce 269.54 kg/h of liquid biomethanol. Notably, the system emits approximately 8 kg/h of CO₂, released from the methanol synthesis unit via streams 315 and 324. The carbon dioxide emissions per unit of biofuel production are very low, with an E_{CO_2} value of 0.017 kgCO₂/kg_{biomass}, making the system highly efficient in terms of carbon output and potentially classifiable as a low-carbon emission system.

Table 4 illustrates the distribution of power supplied and consumed by the various subsystems. According to the data, the SOEC subsystem accounts for the highest energy consumption, using 86% of the total power, highlighting the need for efficiency improvements in this system. Following the SOEC, the MSU subsystem is the second-largest consumer of electricity, using 13% of the total, primarily for operating the compressors. The anaerobic digestion and biogas upgrading subsystems have significantly lower power demands, consuming less than 1% due to the lower energy requirements of the pump compared to the compressor. It is also important to note that the electricity supply for the overall system is provided by a combination of the gas turbine in the oxy-fuel unit and the renewable energy sources.

Table 4. Power suppliers and consumption of the proposed system.

Parameter	Unit	Value
Power generation of RES for the overall system	kW	949.7
Power generation of the oxy-fuel gas turbine unit	kW	10.1
Power consumption of the biogas upgrading unit	kW	−0.77
Power consumption of the anaerobic digestion unit	kW	−5.38
Power consumption of MSU	kW	−129.43
Power consumption of SOEC	kW	−824.89

4.3. Performance Comparison

This subsection evaluates the overall results of the system in comparison with previous studies focused on producing biomethanol and biomethane from biogas fuel. Rinaldi et al. (2023) [40] investigated biogas conversion into methanol using a steam reforming process. The study focused on a 20 MW_{LHV} biogas to methanol process designed to treat biogas produced via anaerobic digestion of municipal solid waste. The authors explored three different process configurations varying the presence and position of the carbon dioxide separation unit: upstream of the reformer, downstream of the reformer, and no separation. The best results were achieved with CO₂ separation performed upstream of the reformer, which allowed for higher carbon and fuel efficiencies. The analysis revealed that this configuration produced 2480 kg/h of methanol, fuel efficiencies, emitted CO₂, and electric consumption per methanol produced 72.2%, 1.23, and 1.99 MJ/kg, respectively. By comparing these results with the same amount of fuel of 0.167933 kg/s, the power consumption is 245.2 kW, and the methanol production is 441 kg/h without methane production.

In another similar study by Ghosh et al. (2023) [41], the authors present a detailed analysis focusing on the production of methanol from biogas generated via the anaerobic digestion of municipal solid waste. The process they designed employs steam reforming to convert biogas into syngas (synthesis gas), which is then used to synthesize methanol. The analysis covers three different configurations of the carbon dioxide separation unit: before the reformer, after the reformer, and with no separation. The analysis revealed that the third configuration has high methanol productivity, which allowed for the production of 24.31 kg/s methanol and rich carbon dioxide off gas from 28.99 kg/s biogas. These values have been changed to comparable values with the present work and are shown in Table 5.

Table 5. Comparison of the overall results of the proposed system with other biogas-to-methanol systems.

	Unit	Ref. [40]	Ref. [41]	Present Work BSOF = 20%	Present Work BSOF = 100%
Biogas input	kg/s	0.167933	0.167933	0.167933	0.167933
Power consumption	kW	245.2	213	949.7	4534.3
Heat consumption	kW	NA	NA	839.38	0
Heat generation	kW	0	0	0	2313
Methanol production	kg/h	441	507	269.54	590.1
Methane production	kg/h	0	0	188.68	0
Purity of the produced methanol	%	99.5	99.2	99.48	99.48
Purity of the produced methane	%	-	-	98	-
Emitted CO ₂ per Biofuel production, ECO ₂	-	1.23	0.392	0.01742	0.01694

Biogas Split fraction into the Oxy-fuel gas turbine unit = BSOF.

Table 5 provides a comparative analysis of the proposed biogas-to-methanol conversion system against two referenced systems (Refs. [40,41]). The study examines two scenarios within its framework: a base scenario, where the biogas split fraction into the oxy-fuel gas turbine unit (BSOF) is set at 20%, and an alternative scenario, focused solely on methanol production with a BSOF value of 100%. Comparing the biomethanol production of the present system with Refs. [40,41], in the basic mode, the present system produces biomethane in addition to the production of biomethanol, and in the case of BSOF = 100%, only biomethanol production is considered; the amount of biomethanol produced is more than Refs. [40,41]. It should also be noted that the amount of heat consumed has not been reported in Refs. [40,41], although it needs a significant amount of heat to produce biogas from biomass in aerobic digestion.

The findings indicate that in the current system, carbon dioxide emissions are about 70 and 23 times lower than those reported in Refs. [40,41], respectively. This reduction is attributed to using the SOEC system, which results in significantly reduced carbon dioxide emissions despite its high energy consumption for separating hydrogen and oxygen from water.

4.4. Sensitivity Analysis

This section outlines the principal results concerning the impact of the biogas split fraction on the oxy-fuel gas turbine unit. This study evaluates five objective functions: energy efficiency, power consumption, heat consumption, biomethane production, and biomethanol production.

Figure 7 illustrates the impact of the methanol reactor temperature on the energy efficiency, power and heat consumption, and the capacities for biomethane and biomethanol production. Figure 7 indicates that as the reactor temperature is increased from 220 °C to 280 °C, the rate of methanol production in the reactor increases due to the chemical reactions occurring. This increase enhances methanol output in the production system. Additionally, the results show that elevating the reactor temperature indirectly lowers the flow rate of gas through the CP3 compressor, which in turn reduces power consumption—evidenced by the descending trend in the power consumption graph. Consequently, the reactor temperature appears not to be affected by the biogas upgrading unit, resulting in steady heat consumption and methane production capacity. Ultimately, with a significant increase in methanol production and a decrease in the power consumption of the entire system, the energy efficiency of the system increases significantly.

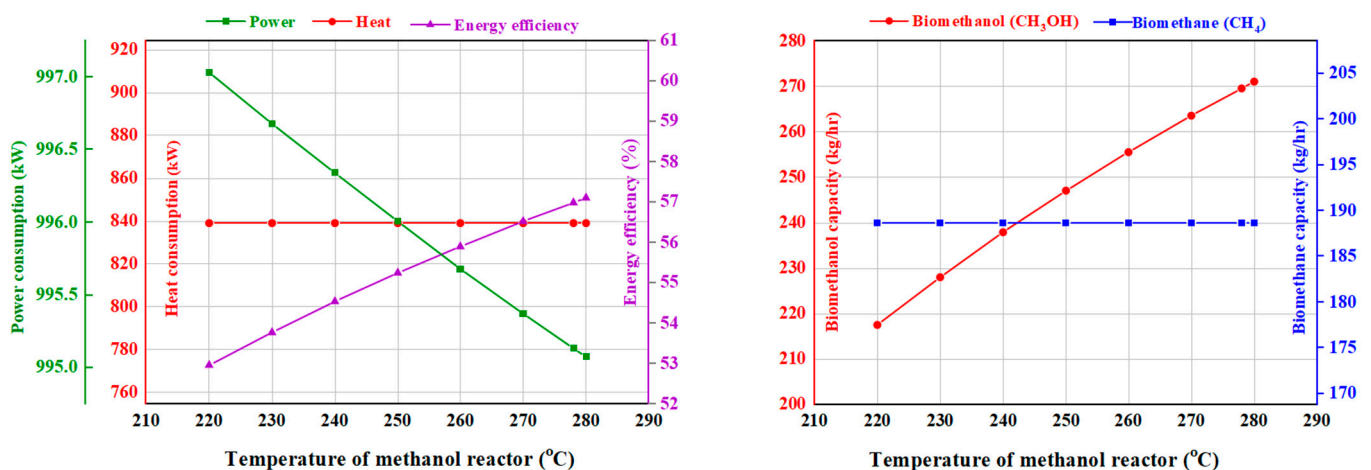


Figure 7. Impact of the temperature of methanol reactor on the performance of the proposed system.

Figure 8 illustrates the impact of the pressure of the oxy-fuel combustion chamber unit (PCC) on the energy efficiency, power and heat consumption, and the capacities for biomethane and biomethanol production. According to the figure shown, with an increase in PCC, a maximum efficiency point appears. This fact can be explained by the observation that as PCC increases from 3 to 6 bar, the power generated by the turbine in the oxy-fuel gas turbine unit outweighs the power consumed by the compressor in the same unit, leading to an increase in the power output of the oxy-fuel gas turbine unit. However, when PCC increases from 6 to 10 bar, the opposite scenario occurs. This is why the total system power consumption has a minimum point at approximately 6 bar pressure. Conversely, the total system heat consumption behaves in the opposite manner. It should be noted that the impact of the system's power consumption on the energy efficiency is greater than that of the total system heat consumption; therefore, the maximum efficiency point occurs at about 6 bar pressure.

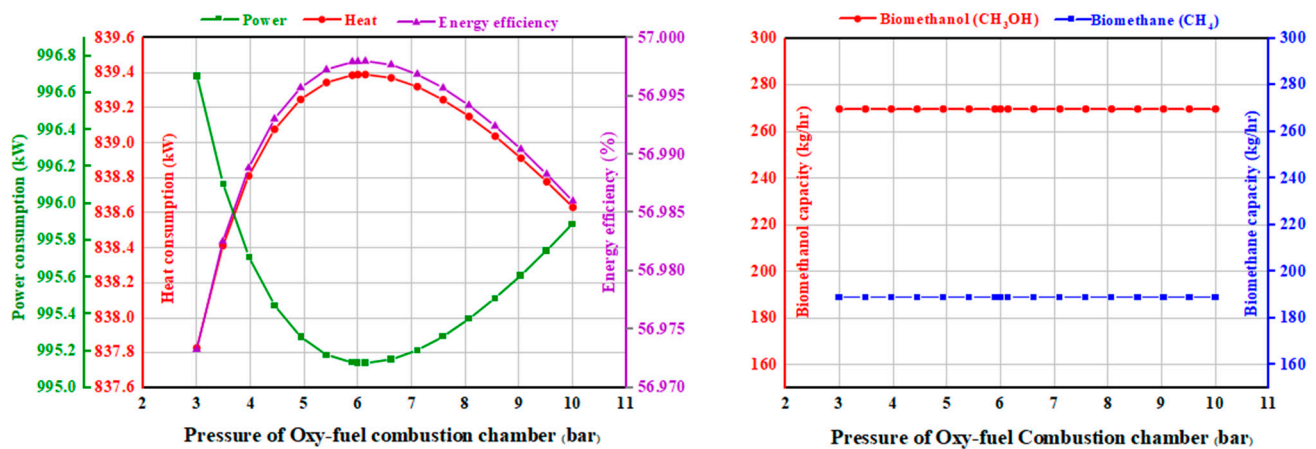


Figure 8. Impact of pressure of the oxy-fuel combustion chamber on the performance of the proposed system.

4.5. Projected Price of Green Methanol

Although a full techno-economic analysis is planned as part of future research, it is possible to provide a preliminary projection of the potential price impact of producing green methanol using the optimized system. Currently, green methanol is priced at a premium due to the costs associated with renewable energy inputs and advanced technologies. In our integrated system, the Solid Oxide Electrolysis Cell plays a crucial role in driving the production of hydrogen, which is essential for methanol synthesis, but it is also a high-energy-demanding unit. This increased energy consumption may raise production costs unless offset by using low-cost renewable energy sources such as solar or wind.

Based on the high purity of the biomethanol (99.48%) produced in this system, the premium pricing could still be justified in niche markets such as the shipping industry, which is increasingly adopting green fuels to meet decarbonization targets. Additionally, the system's environmental benefits, including significant reductions in carbon emissions, position it as a competitive solution for industries focused on sustainability. A detailed cost breakdown, including capital expenditures (CAPEX) and operational expenditures (OPEX), will be part of future research using techno-economic models to quantify the costs associated with construction, operation, and maintenance.

5. Conclusions

This study proposes new solutions for biomethanol and biomethane production units, examined with thermodynamics. The key findings are summarized below:

- The system achieves an overall energy efficiency of 58.09%, converting input energy to biofuel outputs, with the main power consumers being the SOEC and methanol synthesis units, requiring 824 kW and 124 kW, respectively.
- Processing 30,988.8 kg/h of biomass, the system produces 188.68 kg/h of biomethane and 269.54 kg/h of biomethanol, with 23.2 kg/h of hydrogen supplied to the methanol unit from the SOEC. Increasing the reactor temperature from 220 °C to 280 °C improves energy efficiency from 53.7% to 57.3%.
- The SOEC system, consisting of three blocks of 80 cells each, generates 23.2 kg/h of hydrogen and 184 kg/h of oxygen. Adjusting the reactor temperature and bio-gas split fraction impacts methanol production, power consumption, and overall system efficiency.
- The system emits 0.017 kg of CO₂ per unit of biofuel, making it a low-emission system, with the SOEC as the highest energy consumer, presenting opportunities for optimization to improve efficiency.

The challenges of the proposed system are that our results are influenced by several factors, including modeling assumptions such as steady-state operation and ideal gas behavior, which may not fully capture real-world performance. The analysis focuses on a small to medium scale and does not extensively explore the variability of renewable energy sources. Future advancements in market trends and environmental sustainability could lead to changes in background systems that are beyond this study's scope but offer potential for further research. A key challenge is the high energy demand of the Solid Oxide Electrolysis Cell, which could be addressed by integrating more renewable energy or improving SOEC efficiency. Additionally, advancements in technology and environmental policies may impact the conversion of sewage sludge to biomethanol and natural gas, influencing system performance and scalability.

The integrated system offers several key advantages, including the high purity of both biomethanol (99.48%) and biomethane (98%), which enhances their market value and suitability for industrial applications. The system is powered by renewable energy sources, reducing its carbon footprint and reliance on fossil fuels. Additionally, the production of biomethanol, a high-value product used in chemical industries and as a clean fuel, particularly in the shipping sector, adds significant economic value. These combined benefits make the system both environmentally sustainable and economically viable.

For future research, the proposed biofuel plant will be evaluated through both techno-economic assessments and environmental analysis. Techno-economic assessments will utilize cost functions and EES software V10 to calculate construction, operational, and maintenance costs. Simultaneously, a Life Cycle Assessment (LCA) will be conducted to quantify the environmental impacts of the plant. Additionally, future work should focus on scaling up the system, optimizing its performance, and incorporating dynamic modeling to reflect real-world conditions. Expanding the LCA to other geographical regions and integrating the system with Fischer-Tropsch biofuels could enable the production of additional fuels such as gasoline, jet fuel, and diesel. These research directions will enhance the system's commercial viability and provide a comprehensive understanding of its long-term economic and environmental implications.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Nomenclature

4SCP	Four stage compressors
ADU	Anaerobic digestion unit
BUU	Biogas upgrading unit
BSOF	Biogas split fraction into the oxy-fuel gas turbine unit
Comp	Compressor
D^{eff}	Effective diffusion (m^2/s)
E_{act}	Activation energy (J/mol)
ECO	Economizer
EVA	Evaporator
F	Faraday's constant ($^\circ\text{C}/\text{mol}$)
FG	Flue gas
GHG	Greenhouse gases
GT	Gas turbine
h	Enthalpy (kJ/kg)
HRSG	Heat recovery steam generator
HX	Heat exchanger
J	Current density (A/m^2)
LHV	Lower heating value (kJ/kg)
LCA	Life Cycle Assessment
M	Mixer
$\dot{m}$	Mass flow rate (kg/h)
Met	Methanol
MSU	Methanol Synthesis Unit
N_{cell}	Number of cells
$\dot{n}$	Mole flow rate (mol/s)
NGT	Natural gas turbine
P	Pressure (bar)
p^0	Partial pressure (bar)
PCC	Pressure of the oxy-fuel combustion chamber unit
P2X	Power-to-X

Greek letters

$\dot{Q}$	Heat transfer rate (kW)
R	Ideal gases constant ($\text{J}/\text{mol}/\text{K}$)
RES	Renewable energy sources
SOEC	Solid Oxide Electrolysis Cell
T	Temperature ($^\circ\text{C}$)
V	Voltage (V)
WAT	Water
$\dot{W}$	Electric power (kW)
δ	Thickness (m)
η	Efficiency (%)
γ	Pre-exponential factor

Subscripts

a	Anode
act	Activation
c	Cathode

cell	SOE cell
Comp	Compressor
conc	Concentration
CP	Compressor
e	Electrolyte
en	Energy
i	Anode, cathode, or electrolyte
in	Input
N	Nernst equation
Ohm	Ohmic
out	Output
REB	Reboiler

Appendix A

Table A1. Elemental analysis of the organic components in the sewage sludge [21].

Element	C	H	O	N	S	Ash	LHV
Weight percentage	35.65%	4.89%	21.72%	5.16%	2.97%	29.61%	5000 kJ/kg

Table A2. Parameters and operating conditions for the thermophilic anaerobic digestion of the sewage sludge [21].

Parameter	Details/Value
Dry Matter Content of Sludge	33.56 g/L
Volatile Solids (VS) content	25.9 g/L
Biodegradability of the sewage sludge	(38.1 ± 1.4)%
Specific biogas yield	(285.89 ± 10.6) [NL/kg]
Average methane content	(64.26 ± 1.55)%
Methane productivity of the sewage sludge	(0.387 ± 0.017) m ³ /m ³ . d
Mass flow rate of biomass	8.608 kg/s
Biogas production of the anaerobic digestate	0.167933 kg/s
Efficiency of the biogas production process (mass biogas produced per mass biomass consumed)	1.951%
Operating temperature of the AD reactor	55 °C (thermophilic conditions)
Operating temperature of the thermal pretreatment	90 °C (thermophilic conditions)
Retention duration for the anaerobic digestion	12 days
Gas composition of biogas	36.09% CO ₂ , 62.26% CH ₄ , and 1.65% H ₂ O under thermophilic conditions
pH of the AD Reactor	7.1–7.3 (maintained for optimal biogas production)
Number of the anaerobic digesters	4
Total volume of the anaerobic digesters	12,000 m ³
Gas leakage consideration	Stainless steel connectors sealed by silicon gaskets were used to prevent biogas leaks

Municipal sewage sludge underwent thermophilic anaerobic digestion after a 0.5-h thermal pretreatment at 90°C.

Table A3. Thermodynamic properties of the state points of the ADU system.

State	T (°C)	P (bar)	$\dot{m}$ (kg/h)	$\dot{n}$ (kmol/h)	Mole Fraction (%)		
					CO ₂	H ₂ O	CH ₄
101	18	1.06	30,988.8	1720.14	0	100	0
102	48.5	1.01	30,988.8	1720.14	0	100	0
103	48.52	2	30,988.8	1720.14	0	100	0
104	78	1.95	30,988.8	1720.14	0	100	0
105	90	1.1	30,988.8	1720.14	0	100	0
106	90.05	3.54	30,988.8	1720.14	0	100	0
107	60.63	3.34	30,988.8	1720.14	0	100	0
108	55	1.68	30,384.24	1686.58	0	100	0
109	55.00	1.48	30,384.24	1686.58	0	100	0
110	23.89	1.48	604.560	23.1025	32.87	10.42	56.71
111	55.00	1.48	604.560	23.1025	32.89	10.37	56.74
112	55.00	1.48	604.560	23.1025	36.09	1.65	62.26
113	19	1.48	120.912	4.6205	36.09	1.65	62.26
114	19	1.48	483.648	18.482	36.09	1.65	62.26

Table A4. Thermodynamic properties of the state points of the SUEC system.

State	T (°C)	P (bar)	$\dot{m}$ (kg/h)	$\dot{n}$ (kmol/h)	Mole Fraction (%)		
					H ₂ O	O ₂	H ₂
201	25	1	207.300	11.507	100	0	0
202	750	1	207.300	11.507	100	0	0
203	750	1	124.380	6.904	100	0	0
204	750	1	331.680	18.411	100	0	0
205	750	1	16.397	2.046	37.5	0	62.5
206	750	1	348.077	20.457	93.75	0	6.25
207	750	1	348.077	26.210	29.268	21.951	48.780
208	750	1	184.103	5.753	0	100	0
209	750	1	163.974	20.457	37.5	0	62.5
210	750	1	147.576	18.411	37.5	0	62.5
211	750	1	23.197	11.507	0	0	100
212	100	1	23.197	11.507	0	0	100
213	100	1	184.103	5.753	0	100	0

Table A5. Thermodynamic properties of the state points of the MSU system.

State	T (°C)	P (bar)	$\dot{m}$ (kg/h)	$\dot{n}$ (kmol/h)	Mole Fraction (%)				
					CO ₂	H ₂ O	H ₂	CO	CH ₃ OH
301	156.8	51	23.197	11.507	0	0	100	0	0
302	33.53	1	501.929	11.683	95.970	4.030	0	0	0
303	125.60	51	501.929	11.683	95.970	4.030	0	0	0
304	128.88	51	525.126	23.190	48.350	2.030	49.620	0	0
305	43.28	51	1331.995	115.894	11.634	0.081	70.722	17.235	0.328
306	58.15	51	1857.120	155.544	17.036	0.372	72.207	10.122	0.262
307	210.05	49.98	1857.120	155.544	17.036	0.372	72.207	10.122	0.262
308	278.00	49.98	1857.120	138.825	9.872	9.633	59.644	14.535	6.315
309	143.06	48.98	1857.120	138.825	9.872	9.633	59.644	14.535	6.315
310	136.02	48	1857.120	138.825	9.872	9.633	59.644	14.535	6.315
311	109.00	48	1857.120	138.825	9.872	9.633	59.644	14.535	6.315
312	35.05	47.04	1857.120	138.825	9.872	9.633	59.644	14.535	6.315
313	35.05	47.04	511.535	21.749	0.385	61.052	0.013	0.005	38.544
314	32.05	1.2	511.535	21.749	0.385	61.052	0.013	0.005	38.544
315	32.05	1.2	3.227	0.079	83.838	2.252	3.618	1.350	8.942
316	32.05	1.2	508.308	21.669	0.079	61.268	0	0	38.653
317	80.05	1.176	508.308	21.669	0.079	61.268	0	0	38.653
318	102.52	1	238.725	13.251	0	99.994	0	0	0.006
319	40.00	1	238.725	13.251	0	99.994	0	0	0.006
320	64.54	1	269.583	8.419	0.203	0.315	0	0	99.481
321	77.67	1.2	269.583	8.419	0.203	0.315	0	0	99.481
322	40.05	1.176	269.583	8.419	0.203	0.315	0	0	99.481
323	35.05	47.04	1345.585	117.076	11.634	0.081	70.722	17.235	0.328
324	35.05	47.04	13.590	1.182	11.634	0.081	70.722	17.235	0.328
325	35.05	47.04	1331.995	115.894	11.634	0.081	70.722	17.235	0.328

Table A6. Thermodynamic properties of the state points of the Oxy-fuel gas turbine unit.

State	T (°C)	P (bar)	$\dot{m}$ (kg/h)	$\dot{n}$ (kmol/h)	Mole Fraction (%)			
					CO ₂	H ₂ O	O ₂	CH ₄
401	55.46	1	305.015	10.374	16.074	0.735	55.461	27.730
402	290.90	6	305.015	10.374	16.074	0.735	55.461	27.730
403	1022.44	6	2033.435	69.160	43.805	56.195	0	0
404	1022.44	6	1728.420	58.786	43.805	56.195	0	0
405	724.60	6	1728.420	58.786	43.805	56.195	0	0
406	431.92	6	1728.420	58.786	43.805	56.195	0	0
407	300	6	1728.420	58.786	43.805	56.195	0	0
408	1022.44	6	305.015	10.374	43.805	56.195	0	0
409	777.60	1	305.015	10.374	43.805	56.195	0	0

Table A6. Cont.

State	T (°C)	P (bar)	$\dot{m}$ (kg/h)	$\dot{n}$ (kmol/h)	Mole Fraction (%)			
					CO ₂	H ₂ O	O ₂	CH ₄
410	100	1	305.015	10.374	43.805	56.195	0	0
411	35	1	305.015	10.374	43.805	56.195	0	0
412	35	1	203.629	4.746	95.740	4.260	0	0
413	35	1	101.386	5.628	0.002	99.998	0	0
414	37.5	1.5	298.300	6.937	96.128	3.872	0	0

Table A7. Thermodynamic properties of the state points of the biogas upgrading unit.

State	T (°C)	P (bar)	$\dot{m}$ (kg/h)	$\dot{n}$ (kmol/h)	Mole Fraction (%)					
					MEA	CO ₂	CH ₄	H ₂ O	MEACOO–	MEA+
501	19.00	1.5	483.648	18.482	0.000	36.09	62.26	1.650	0	0
502	216.97	10	483.648	18.482	0.000	36.09	62.26	1.650	0	0
503	20.00	1.05	7604.340	333.028	11.153	0	0	88.777	0	0.035
504	20.00	1.05	188.687	11.733	0.001	0	98.05	1.950	0	0
505	43.64	1.05	7899.256	333.132	7.215	0.007	0.001	88.742	1.930	2.039
506	43.72	1.5	7899.256	333.107	7.201	0	0.001	88.748	1.938	2.047
507	76.53	1.5	7899.256	333.107	7.218	0	0.001	88.756	1.946	2.022
508	37.18	1.5	298.301	6.934	0.003	95.44	0.041	4.520	0	0
509	115.49	1.5	7601	332.843	11.163	0	0	88.772	0	0.033
510	84.26	1.5	7601.000	332.843	11.16	0	0	88.768	0	0.036
511	25.00	1.05	3.340	0.185	0.13	0	0	99.864	0	0.003
512	84.23	1.05	7604.340	333.028	11.152	0	0	88.776	0	0.036

References

1. Gholizadeh, T.; Ghiasirad, H.; Skorek-Osikowska, A.; Arabkoohsar, A. Techno-economic optimization and working fluid selection of a biogas-based dual-loop bi-evaporator ejector cooling cycle involving power-to-hydrogen and water facilities. *Int. J. Hydrogen Energy* **2024**, *76*, 247–262. [\[CrossRef\]](#)
2. Gholizadeh, T.; Ghiasirad, H.; Rostami, S.; Skorek-Osikowska, A. A biogas-fired cogeneration (cooling and power) system combined with biomethane facilities: 3E evaluation, sensitivity analyses and optimization. *Environ. Dev. Sustain.* **2024**, 1–53. [\[CrossRef\]](#)
3. Baris, T.G.; Ghiasirad, H.; Megdouli, K.; Anvari, S.; Stanek, B.; Skorek-Osikowska, A.; Bartela, L. Transient exergy analysis of ejector cooling and thermoelectric generator systems using heat storage and parabolic trough collector for residential buildings. *J. Physics Conf. Ser.* **2023**, *2600*, 062009. [\[CrossRef\]](#)
4. Gholizadeh, T.; Vajdi, M.; Rostamzadeh, H. Exergoeconomic optimization of a new trigeneration system driven by biogas for power, cooling, and freshwater production. *Energy Convers. Manag.* **2020**, *205*, 112417. [\[CrossRef\]](#)
5. Gholizadeh, T.; Vajdi, M.; Mohammadkhani, F. Thermodynamic and thermoeconomic analysis of basic and modified power generation systems fueled by biogas. *Energy Convers. Manag.* **2019**, *181*, 463–475. [\[CrossRef\]](#)
6. Nemmour, A.; Inayat, A.; Janajreh, I.; Ghenai, C. Green hydrogen-based E-fuels (E-methane, E-methanol, E-ammonia) to support clean energy transition: A literature review. *Int. J. Hydrogen Energy* **2023**, *48*, 29011–29033. [\[CrossRef\]](#)
7. AlZahrani, A.A.; Dincer, I. Modeling and performance optimization of a solid oxide electrolysis system for hydrogen production. *Appl. Energy* **2018**, *225*, 471–485. [\[CrossRef\]](#)
8. Daneshpour, R.; Mehrpooya, M. Design and optimization of a combined solar thermophotovoltaic power generation and solid oxide electrolyser for hydrogen production. *Energy Convers. Manag.* **2018**, *176*, 274–286. [\[CrossRef\]](#)
9. Schiller, G.; Lang, M.; Szabo, P.; Monnerie, N.; von Storch, H.; Reinhold, J.; Sundarraj, P. Solar heat integrated solid oxide steam electrolysis for highly efficient hydrogen production. *J. Power Sources* **2019**, *416*, 72–78. [\[CrossRef\]](#)
10. Leonzio, G.; Zondervan, E.; Foscolo, P.U. Methanol production by CO₂ hydrogenation: Analysis and simulation of reactor performance. *Int. J. Hydrogen Energy* **2019**, *44*, 7915–7933. [\[CrossRef\]](#)

11. Parigi, D.; Giglio, E.; Soto, A.; Santarelli, M. Power-to-fuels through carbon dioxide Re-Utilization and high-temperature electrolysis: A technical and economical comparison between synthetic methanol and methane. *J. Clean. Prod.* **2019**, *226*, 679–691. [\[CrossRef\]](#)
12. Rivera-Tinoco, R.; Farran, M.; Bouallou, C.; Auprêtre, F.; Valentin, S.; Millet, P.; Ngameni, J. Investigation of power-to-methanol processes coupling electrolytic hydrogen production and catalytic CO₂ reduction. *Int. J. Hydrogen Energy* **2016**, *41*, 4546–4559. [\[CrossRef\]](#)
13. Lonis, F.; Tola, V.; Cau, G. Renewable methanol production and use through reversible solid oxide cells and recycled CO₂ hydrogenation. *Fuel* **2019**, *246*, 500–515. [\[CrossRef\]](#)
14. Zhang, H.; Desideri, U. Techno-economic optimization of power-to-methanol with co-electrolysis of CO₂ and H₂O in solid-oxide electrolyzers. *Energy* **2020**, *199*, 117498. [\[CrossRef\]](#)
15. Ostadi, M.; Bromberg, L.; Cohn, D.R.; Gençer, E. Flexible methanol production process using biomass/municipal solid waste and hydrogen produced by electrolysis and natural gas pyrolysis. *Fuel* **2023**, *334*, 126697. [\[CrossRef\]](#)
16. Moiola, E.; Wötzel, A.; Schildhauer, T. Feasibility assessment of small-scale methanol production via power-to-X. *J. Clean. Prod.* **2022**, *359*, 132071. [\[CrossRef\]](#)
17. Eggemann, L.; Escobar, N.; Peters, R.; Burauel, P.; Stolten, D. Life cycle assessment of a small-scale methanol production system: A Power-to-Fuel strategy for biogas plants. *J. Clean. Prod.* **2020**, *271*, 122476. [\[CrossRef\]](#)
18. Riaz, A.; Chaniago, Y.D.; Hussain, A.; Andika, R.; Kim, G.; Lim, H.; Lee, M.; Riaz, A.; Chaniago, Y.D.; Hussain, A.; et al. Thermodynamic, economic, and emissions assessment of integrated power to methanol concept with membrane-based biogas up-gradation and plasma electrolysis. *J. Clean. Prod.* **2022**, *363*, 132367. [\[CrossRef\]](#)
19. Hai, T.; Lin, H.; Albdeiri, M.S.; Alsenani, T.R.; Elattar, S.; Abed, A.M.; Tian, R. A novel trigeneration model using landfill gas upgrading process and waste heat recovery: Application of methanol, desalinated water, and oxygen production. *J. Clean. Prod.* **2023**, *393*, 136224. [\[CrossRef\]](#)
20. Gray, N.; O'Shea, R.; Smyth, B.; Lens, P.N.; Murphy, J.D. What is the energy balance of electrofuels produced through power-to-fuel integration with biogas facilities? *Renew. Sustain. Energy Rev.* **2021**, *155*, 111886. [\[CrossRef\]](#)
21. Mirmasoumi, S.; Saray, R.K.; Ebrahimi, S. Evaluation of thermal pretreatment and digestion temperature rise in a biogas fueled combined cooling, heat, and power system using exergo-economic analysis. *Energy Convers. Manag.* **2018**, *163*, 219–238. [\[CrossRef\]](#)
22. Vilardi, G.; Bassano, C.; Deiana, P.; Verdone, N. Exergy and energy analysis of three biogas upgrading processes. *Energy Convers. Manag.* **2020**, *224*, 113323. [\[CrossRef\]](#)
23. Nugroho, Y.K.; Zhu, L.; Heavey, C. Building an agent-based techno-economic assessment coupled with life cycle assessment of biomass to methanol supply chains. *Appl. Energy* **2022**, *309*, 118449. [\[CrossRef\]](#)
24. Ghiasirad, H.; Skorek-Osikowska, A. Biomethanol production via electrolysis, oxy-fuel combustion, water-gas shift reaction, and LNG cold energy recovery. *Int. J. Hydrogen Energy* **2024**, *52*, 610–626. [\[CrossRef\]](#)
25. Megdouli, K.; Gholizadeh, T.; Tashtoush, B.; Cinnella, P.; Skorek-Osikowska, A. Optimization of carbon dioxide ejector expansion transcritical refrigeration system with ANOVA and NSGA-II. *Int. J. Refrig.* **2024**, *158*, 173–189. [\[CrossRef\]](#)
26. Gholizadeh, T.; Vajdi, M.; Rostamzadeh, H. A new biogas-fueled bi-evaporator electricity/cooling cogeneration system: Exergoeconomic optimization. *Energy Convers. Manag.* **2019**, *196*, 1193–1207. [\[CrossRef\]](#)
27. Çengel, Y. *Thermodynamics: An Engineering Approach*; McGraw-Hill: New York, NY, USA, 2004.
28. Milewski, J.; Kupecki, J.; Szczeńiak, A.; Uzunow, N. Hydrogen production in solid oxide electrolyzers coupled with nuclear reactors. *Int. J. Hydrogen Energy* **2020**, *46*, 35765–35776. [\[CrossRef\]](#)
29. AlZahrani, A.A.; Dincer, I. Thermodynamic and electrochemical analyses of a solid oxide electrolyzer for hydrogen production. *Int. J. Hydrogen Energy* **2017**, *42*, 21404–21413. [\[CrossRef\]](#)
30. Habibollahzade, A.; Gholamian, E.; Behzadi, A. Multi-objective optimization and comparative performance analysis of hybrid biomass-based solid oxide fuel cell/solid oxide electrolyzer cell/gas turbine using different gasification agents. *Appl. Energy* **2019**, *233–234*, 985–1002. [\[CrossRef\]](#)
31. Wang, L.; Düll, J.; Maréchal, F.; Van Herle, J. Trade-off designs and comparative exergy evaluation of solid-oxide electrolyzer based power-to-methane plants. *Int. J. Hydrogen Energy* **2018**, *44*, 9529–9543. [\[CrossRef\]](#)
32. Ishaq, H.; Crawford, C. CO₂-based alternative fuel production to support development of CO₂ capture, utilization and storage. *Fuel* **2023**, *331*, 125684. [\[CrossRef\]](#)
33. Eisavi, B.; Ranjbar, F.; Nami, H.; Chitsaz, A. Low-carbon biomass-fueled integrated system for power, methane and methanol production. *Energy Convers. Manag.* **2021**, *253*, 115163. [\[CrossRef\]](#)
34. Bahnamiri, F.K.; Khalili, M.; Pakzad, P.; Mehrpooya, M. Techno-economic assessment of a novel power-to-liquid system for synthesis of formic acid and ammonia, based on CO₂ electroreduction and alkaline water electrolysis cells. *Renew. Energy* **2022**, *187*, 1224–1240. [\[CrossRef\]](#)
35. Zare, A.A.D.; Yari, M.; Mohammadkhani, F.; Nami, H.; Desideri, U. Thermodynamic and exergoeconomic analysis of a multi-generation gas-to-X system based on fuel-rich combustion to produce power, hydrogen, steam and heat. *Sustain. Cities Soc.* **2022**, *86*, 104139. [\[CrossRef\]](#)
36. Tashtoush, B.; Megdouli, K.; Gholizadeh, T.; Dekam, E. Exergoeconomic analyses of a cement plant waste heat recovery in a novel combined power and refrigeration cycle. *Int. J. Des. Nat. Ecodynamics* **2021**, *16*, 251–260. [\[CrossRef\]](#)

37. Gholizadeh, T.; Vajdi, M.; Rostamzadeh, H. Energy and exergy evaluation of a new bi-evaporator electricity/cooling cogeneration system fueled by biogas. *J. Clean. Prod.* **2019**, *233*, 1494–1509. [[CrossRef](#)]
38. Ghiasirad, H.; Baris, T.G.; Javanfam, F.; Kalkhoran, H.R.; Skorek-Osikowska, A. Indirect integration of a thermal–mechanical heat pump with a humidification-dehumidification desalination unit. *Appl. Therm. Eng.* **2023**, *230*, 120852. [[CrossRef](#)]
39. Safari, F.; Dincer, I. Development and analysis of a novel biomass-based integrated system for multigeneration with hydrogen production. *Int. J. Hydrogen Energy* **2019**, *44*, 3511–3526. [[CrossRef](#)]
40. Rinaldi, R.; Lombardelli, G.; Gatti, M.; Visconti, C.G.; Romano, M.C. Techno-economic analysis of a biogas-to-methanol process: Study of different process configurations and conditions. *J. Clean. Prod.* **2023**, *393*, 136259. [[CrossRef](#)]
41. Ghosh, S.; Uday, V.; Giri, A.; Srinivas, S. Biogas to methanol: A comparison of conversion processes involving direct carbon dioxide hydrogenation and via reverse water gas shift reaction. *J. Clean. Prod.* **2019**, *217*, 615–626. [[CrossRef](#)]

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