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Conventional vs. alternative biogas utilizations: An LCA-AHP based comparative study

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ABSTRACT

This study compares the performance and the environmental impacts of three biogas utilization processes: combined heat and power cycle, dimethyl ether production, and methanol production. The processes are evaluated based on key performance indicators and life cycle assessments. Results show that molar methane conversion in the reforming unit is 93% for both dimethyl-ether (DME) and methanol processes. Methanol reactor reports a per-pass hydrogen conversion of 21%. DME production achieves an 89% conversion rate. The chemical pathways exhibit a 33% molar conversion of CO_x, contributing to the conversion of CO₂ into advanced chemicals. The environmental footprint is evaluated through a life cycle assessment. Biogas cogeneration has the lowest global warming potential since DME and methanol production processes are influenced by steam production and electricity intake from the national grid, which relies on fossil fuels. An analytic hierarchy process is employed to assess the overall performance of the processes. DME production performs best with a score of 39%, followed by cogeneration with 31%, and methanol production with 30%. Different case studies are examined by modifying the weight criteria for each impact category. The findings provide that cogeneration and DME technologies perform better in all the iterations.

1. Introduction

The global demand for renewable energy sources has gained significant attention due to increasing concerns about climate change and conventional fossil fuels utilization. Among the possible alternatives biogas is a promising solution due to its sustainable nature, the potential for waste management, and the minimal environmental impact. The European Commission is currently working to promote the use of biogas through a comprehensive regulatory framework, investment incentives, and research and development initiatives (Scarlat et al., 2018). According to the EBA statistical report (2021), biogas can significantly contribute to the transition towards a circular economy by effectively exploiting organic waste streams (EBA, 2021). Similarly, the World Biogas Association (WBA) "Global Potential of Biogas" report (2021) highlights the global potential of biogas, estimating that this source could meet approximately 20% of the current natural gas consumption worldwide (WBA, 2021). In anaerobic bioreactors, biogas is primarily produced through anaerobic digestion of organic materials, such as agricultural residues, food waste, and sewage sludge. This process generates a mixture of gases, mainly methane (CH₄) and carbon dioxide

(CO₂), which can be harnessed as a source of energy. The utilization of biogas as an energy source presents significant environmental benefits as well. According to the Intergovernmental Panel on Climate Change (IPCC) Report 2019, biogas production and utilization can substantially mitigate the greenhouse gases emissions (IPCC, 2019). Furthermore, biogas sludges as composts can reduce the reliance on synthetic fertilizers in ranching, thanks to their high phosphorus content (Doyeni et al., 2021). Biogas is mainly employed in Combined Heat and Power (CHP) and Biomethane Injection Plants (BIP). CHP is a conventional cogeneration cycle to produce heat and electricity. BIP is the biogas purification from CO₂ and other impurities to obtain biomethane (Fedeli and Manenti, 2022). In particular, according to the International Energy Agency (IEA) (Connor et al., 2023), the methane content in biomethane should be at least equal to 97%. The higher appeal of the CHP utilization was initially due to the European government financial incentives offered over the 2007–20 period. However, after the expiration of these economic benefits, the biogas market experienced a considerable decline in terms of investors. In Italy, since 2018, the government has tackled this slowdown by expanding incentives to biomethane plants and, more in general, to biofuels like methanol (MeOH) and dimethyl ether (DME) derived from organic biomaterials. Biogas utilization for producing

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List of abbreviations

AHP	Analytical Hierarchy Process	HP	High Pressure
BIP	Biomethane Injection Plant	HPC	Heat, Power & Chemicals
CAPEX	Capital expenditures	IPCC	Intergovernmental Panel on Climate Change
CHP	Combined Heat & Power	KPI	Key Performance Indicator
CZA	Copper, zinc, alumina	LCA	Life Cycle Assessment
DME	Dimethyl ether	LP	Low Pressure
EBA	European Biogas Association	MP	Medium Pressure
EF	Environmental Footprint	OPEX	Operational EXPENDITURE
ELECNRTL	Electrolyte Non Random Two Liquid	PFR	Plug Flow Reactor
GHG	GreenHouse Gases	SRK	Soave-Redlich-Kwong
GWP	Global Warming Potential	WBA	World Biogas Association
		WHSV	Weight Hourly Space Velocity

advanced fuels, such as methanol and dimethyl ether (DME), is of utmost significance in pursuing sustainable energy solutions. This technology is called Heat, Power, and Chemicals (HPC).

Methanol and DME hold multifaceted importance due to their versatile applications and potential to address critical fuel sector challenges, including the reduction of greenhouse gas emissions and energy diversification. Methanol, a high-octane liquid fuel, exhibits great versatility as it can be employed as a direct substitute for gasoline in internal combustion engines or as a precursor for synthesizing several industrial products (Valera et al., 2022; Tian et al., 2022). Its compatibility with existing infrastructure and engines makes it an attractive option for transitioning away from fossil fuels. Moreover, producing methanol from biogas mitigates the environmental concerns related to conventional fuel manufacturing processes. Dimethyl ether (DME), derived from biogas, plays a prominent role as an advanced fuel due to its similar characteristics to diesel fuel (Ng et al., 1999). Relevant attributes such as high cetane number, excellent combustion characteristics and reduced particulate matter emissions makes DME an appealing alternative for compression-ignition engines. In this way, its utilization helps reducing air pollutants and improving air quality (Vakili et al., 2011). Fig. 1 outlines the simplified pathway for cleaner fuel production, such as biomethanol, starting from biogas feedstock. Minor adjustments to the unit layout diversify the final product. For instance, the dimethyl-ether case study involves an additional dehydration step after methanol production. Recent studies (Rafiee, 2020) explored the synthesis of DME using a single reactor unit that combines methanol production and dehydration with specific hybrid catalysts. These conceptual processes must be tailor-designed according to the capacity of the biogas plant. Therefore, the resulting plant will be different with respect to a conventional bulk synthesis. Methanol and DME synthesis start from the production of bio-syngas from biogas feedstock according to steam methane reforming and dry methane reforming reactions (Eqs. (1) and (2)):



Moreover, the HPC process provides added value to the natural CO₂ content by converting it into biofuel. The reactions for methanol and DME synthesis from bio-syngas (Eqs.(3) and (4)) are provided here below:



In CHP and BIP technologies, CO₂ is not converted in different species, and it is emitted at the system outlet. In the first case, the carbon dioxide emissions are given by the sum of the intrinsic biogas CO₂ content and the CO₂ produced by its combustion according to Equation (7):



In BIP technology, CO₂ emissions primarily derive from the bio-methane use as fuel for vehicles or domestic purposes. Additionally, the greenhouse gas content in the biogas is separated and released into the environment or potentially liquefied. Typical biogas upgrading processes operate at low pressures (0.5–1.5 MPa), whereas CO₂ liquefaction and storage require higher pressures (7–7.5 MPa). Only advanced plants, incorporating a secondary compression step, can effectively capture and store CO₂ (Adnan et al., 2019).

In this research work different alternatives for biogas utilization are described and discussed. Process data such as duties, energy, material streams, and waste useful for environmental analysis were retrieved by means of Aspen tools. Process simulation is indeed well-established tool to collect useful data that could be exploited by a wide range analysis. Saebea et al. (2019) developed a process simulation of bio-dimethyl ether synthesis from biogas tri-reforming to evaluate the CO₂ utilization of the system (Saebea et al., 2019). Then, in 2022, Fedeli et al. performed a conceptual design for bio-dimethyl ether (DME) synthesis from biogas aimed at the environmental impact assessment of the

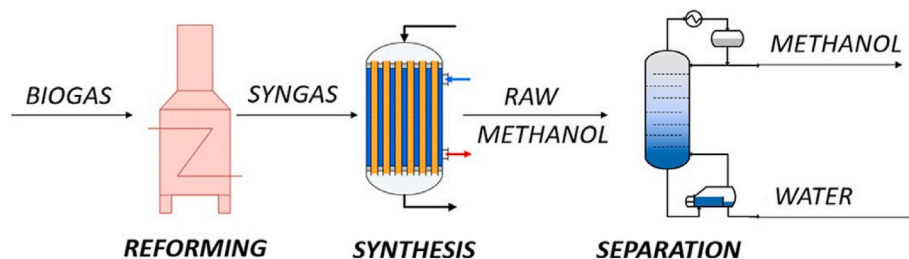


Fig. 1. Simplified scheme of the biofuel production from biogas.

purification section (Fedeli et al., 2022). Oliveria dos Santos et al. (2018) investigated different biogas routes for the production of methanol via mathematical modelling and process simulation. Their results showed palm oil effluent as the highest potential feedstock (Oliveira et al., 2018).

Once completed the process simulation step, a life cycle assessment (LCA) is performed to analyse the environmental impacts of the technologies. The LCA provides a systematic approach to assess the environmental impacts associated with each technology throughout its life cycle, encompassing raw material extraction, production processes, energy use, and waste management. There are several LCA analyses available in literature to evaluate the environmental footprint of biogas utilization whose results can be taken into account as a reference for this study. For instance, Wang et al. (2014) proposed the study of large-scale biogas in China, showing an average of five-time better sustainability than other renewable energy systems. In particular, a better result can be obtained by employing a medium-small capacity plant (Wang et al., 2014). Eggemann et al. (2020) performed an LCA of methanol production from organic waste biogas, highlighting the contribution of this technology to the circular economy (Eggemann et al., 2020). Few works in literature deal with the LCA of DME production from biogas. Among them, the publication where Tomatis et al. (2019) analysed bio-DME production from CO₂ feedstock, not including biogas, could be considered as the most significant outcome since the results highlight a 72% greenhouse gas (GHG) emissions reduction (Tomatis et al., 2019).

In this work, the process with the best features is then identified according to the Analytic Hierarchy Process (AHP). Several Key Performance Indicators (KPIs) are evaluated, including the plant profitability.

The selection of an optimal biogas utilization technology requires a comprehensive evaluation based on environmental, economic, and social considerations.

The Analytical Hierarchy Process (AHP) methodology determines the most suitable technology. AHP is a decision-making tool that allows for the systematic comparison of multiple criteria and facilitates the selection of the most favorable alternative. The criteria considered in this evaluation include greenhouse gas emissions, resource depletion, energy efficiency, operational costs, and social impacts. The AHP method is commonly applied in chemical engineering research in different fields, including biogas applications and its network (Galvez et al., 2015). This analysis is also employed with LCA assessment to evaluate the feasibility and compare several processes or technologies (Wei et al., 2022). Johannesdottir et al. integrated multi-criteria analysis and environmental assessment to evaluate sustainable technical systems for nutrient and carbon recovery from wastewater, including biogas production (Johannesdottir et al., 2021). By conducting the LCA and employing the AHP method, this study aims to identify the most sustainable and economically viable biogas utilization technology. The assessment results will provide valuable insights for stakeholders in the energy sector, policymakers, and investors seeking to promote environmentally friendly and economically feasible biogas utilization practices. Integrating LCA and AHP methodologies in this study ensures a rigorous evaluation framework considering multiple sustainability aspects. By quantifying and comparing the environmental impacts and the economic performance of the different technologies, this research aims to contribute to developing a more sustainable and efficient utilization of biogas.

2. Materials and methods

The three technologies are rigorously simulated in Aspen HYSYS to collect process data for the subsequent environmental assessment. Operating conditions and process flowsheet related to the CHP process are taken from the literature (Dalpaz et al., 2020), since it could be considered a well-established technology. However, DME and methanol production input is taken by the simulation of biogas-to-chemicals

performed in this work. Biogas properties are retrieved from the work of Fedeli and Manenti, which analysed a feedstock from energy crops. The average H₂S content in the gaseous mixture is 200 ppm (Fedeli and Manenti, 2022). The process simulation for this study was performed both with Aspen HYSYS and Aspen Plus software. Further details could be found in the following three sections that present (i) process simulation, (ii) LCA analysis, and (iii) AHP methodology respectively.

2.1. Process simulation

In each technology the process layout accounts for a purification section with equivalent design since the feedstock properties, the inlet flowrate and the operating conditions are the same. Biogas is treated with caustic scrubbing first in order to remove H₂S impurities that could damage the downstreams units by means of corrosion and catalyst poisoning (Chen et al., 2022). Fig. 2 depicts the simplified flowsheet of the scrubbing unit that was rigorously simulated in Aspen Plus with Electrolyte Non Random Two Liquid (ELECNRTL) thermodynamic model. Soave-Redlich-Kwong (SRK) model is selected for the gas phase behaviour. To model this section the ASPEN plus software was used since it is more appropriate to handle electrolytic systems than Aspen HYSYS. The simulation results were then transferred as input parameters in Aspen HYSYS.

From a chemical behaviour perspective, contacting between a mixture of NaOH and H₂O (50% v/v) with raw biogas takes place in the scrubber unit where the formation of sodium sulfate salts occurs according to the following equations.



The sulfide-free biogas with the required purity for further operations exits then from the top of the unit.

The process simulations described below were performed with the NRTL thermodynamic model, implementing the SRK method for the vapor behaviour. Fig. 3 depicts the simplified flowsheet for the first technology, i.e. the biogas cogeneration cycle. Air is compressed through a two-stage intercooler compressor and mixed with biogas before combustion. The combustion heat is then exploited to generate steam at three different conditions: (i) Low Pressure (LP) steam, (ii) Medium Pressure (MP) steam, and (iii) High Pressure (HP) steam. In MP and HP turbines steam and exhaust air expansion are used for electricity

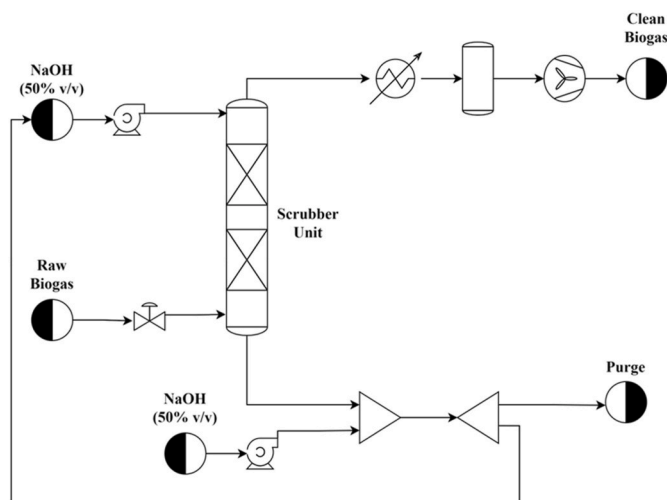


Fig. 2. Biogas purification unit with caustic scrubbing technology.

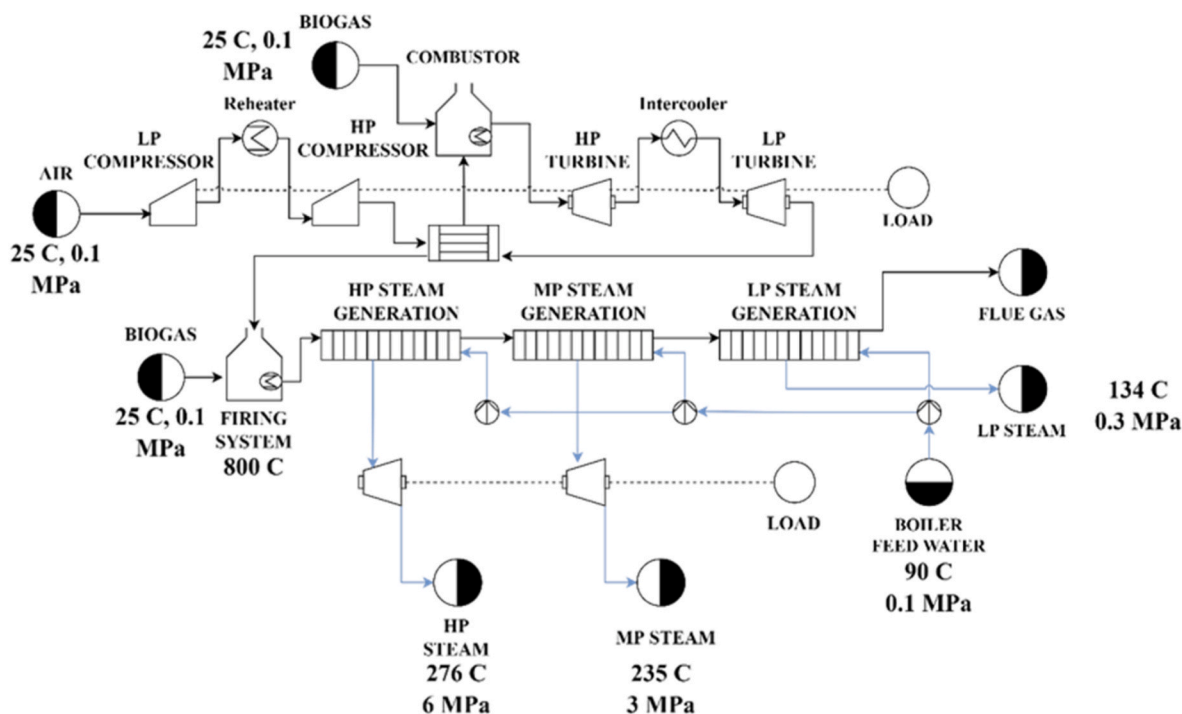


Fig. 3. Simplified flowsheet of biogas cogeneration technology.

generation. The outlet gases from the gas turbine are then mixed and burned with additional biogas in a second firing system to increase the overall temperature.

After that, Aspen HYSYS v11 was used to simulate the CHP cycle. In this second case study air and biogas are directly mixed in the burner. The unit is modelled with a Gibbs reactor, which provides the outlet composition that minimizes the Gibbs free energy. Methane oxidation occurs in the internal chamber where the temperature increases due to the exothermicity of the reaction. The hot flue gases exit from the top of the reactor and enter a process-process heat exchanger. In this unit, the flue gases release heat to high-pressurized liquid water (at 6 MPa) to generate HP steam. In this way, the HP steam is expanded to produce electricity through a turbine.

Methanol and DME production sections are rigorously simulated in Aspen HYSYS v11 as well. In general, the two simulations are rather similar; the main differences can be detected in the downstream section and in the final product. In the proposed layout three different sections can be distinguished: (i) biogas reforming, (ii) methanol/DME production, and (iii) purification section. The first section, where biogas is reformed with steam to produce syngas, is the same for both production pathways. Biogas is fed into the system, and it is compressed with a three-stage compressor up to 1.5 MPa. The pressurized stream is then mixed with MP steam coming from an internal loop. The mixture passes in a process-process heat exchanger where it is pre-heated before entering the steam reforming tubes. This unit is modelled by means of the Aspen HYSYS isothermal Plug Flow Reactor (PFR) module with Xu-Froment kinetics (Xu and Froment, 1989). Inside the catalytic tubes, the following reactions occur (Eqs.(12) and (13)):



The operating conditions of the reformer unit are 950 °C and 1.5 MPa. The outlet syngas heats up the biogas-water mixture and then it is cooled down through a heat exchanger. In this unit, the heat is exploited to generate MP steam (at 1.5 MPa) from the pumped water. Cooled

syngas is dewatered in a separator and the condensed water is recycled back into the water loop for steam generation. Furthermore, dry reformat is sent to a dual-stage compressor (at 6 MPa) for the synthesis sections. The first part of this section is equal for both the synthesis. Dry syngas is pre-heated through two heat exchangers and fed into methanol reactor tubes at 235 °C. This unit is modelled as catalytic PFR with the Graaf refitted kinetics model from the work of Bisotti et al. (2021) (Bisotti et al., 2021). Eqs. (3) and (4) properly describe the system of reactions. Pressure drops of 200 kPa are estimated with the Ergun equation (Towler and Sinnott, 2021). However, the produced methanol is rich in water and light gases such as CO, H₂, CH₄, and CO₂. The uncondensable gases are separated in a water-cooled vessel and recycled back to the reactor to enhance the overall conversion.

At this point of the section, two different process layouts should be designed according to the specific chemical to produce. In the case of methanol production, the liquid mixture exiting the vessel is expanded through a lamination valve down to 0.2 MPa. This pressure falls within the range of the conventional methanol distillation columns. The stream is then fed to a light-end column at 40 °C temperature. In this unit, traces of light gases are removed and sent to a washing column for an additional recovery of the evaporated methanol. This stream is then mixed with the bottom stream of the light-end distillation, resulting in a mixture of methanol and water. The last column separates these compounds operating at a top temperature equal to 76 °C. AA-grade methanol is finally collected from the top of the unit.

Concerning DME synthesis, methanol is pumped up to 1 MPa after the purification section and heated up to 230 °C before entering the DME reactor where the reaction (Eq. (6)) takes place. Even in this case the hot outlet products are useful to pre-heat the reacting mixture. From a simulation perspective, this unit was modelled as an Aspen Gibbs reactor to estimate the equilibrium behaviour of the system. The Aspen Gibbs reactor module is conceived to achieve the equilibrium conditions accounting also for thermodynamics non-idealities. This choice is widely established in literature and some examples can be found in Merkouri et al. (2022) that assessed the DME production by using an Aspen equilibrium reactor (Merkouri et al., 2022) as well as in the work of Moura et al. (2023), where DME production via sugarcane bagasse

gasification is analysed (Moura et al., 2023).

In the process simulation, the outlet stream from the DME converter is mainly composed of DME, water, and unreacted methanol. The first one is separated from the other compounds in the DME purification column working at 160 °C and 1 MPa. To be more precise, DME with ASTM D7901-14 standard specification is collected from the top of the unit, while the water-methanol mixture is recycled back to the methanol column. Figs. 4–5 show the process simulation flowsheet for the productions of methanol and DME, respectively. Despite the use of two different software for this section, the same NRTL thermodynamic model and SRK equation for the gas phase behaviour were kept ensuring good consistency in the results, especially for the methanol/DME separation.

2.2. LCA analysis

Based on the simulations, the LCA analysis of the three processes was then performed employing SimaPRO 9.3 software. A cradle-to-gate lifecycle model was selected as the method to analyse the systems. This methodology assesses the product footprint until it leaves the factory gates before it is transported to the consumer. $1 \text{ m}^3/\text{h}$ of biogas with an average composition of 60% methane and 40% carbon dioxide at atmospheric conditions is used in this LCA study as the functional unit. Nine (9) LCA inventories were created to model the different processes to better organize the data and to avoid a single inventory file with too many inputs and outputs. The biogas purification is a common step for the three technologies. In this section, fertiliser production has been considered as avoided product lowering the impact of this technology. Indeed, the digestate coming from anaerobic digestion is rich in nitrogen, phosphorous, and potassium (Grandas Tavera et al., 2023). Table 1 describes the different inventories and technologies used to make the LCA assessments properly. In order to have the same geographical context as the biogas, the Italian national grid was taken as the reference for electricity intake. The Italian fossil fuel mix states 79%, according to the official report of the IEA agency (IEA and Italy, 2020). Input and output data magnitude were retrieved from the data generated in the process simulation while most of the inventory inputs/outputs were taken from SimaPro databases of the European Market. A detailed description of the inventory is shown in Appendix Section A.

Since bio-syngas production involves the combustion of natural gas to thermally sustain the reactions, this option was added to the market for heating for natural gas. Each distillation column works with steam as a reboiler duty. In this way, steam for the chemical industry is utilised to produce methanol and DME. In inventory n.3, CO_2 was considered as an avoided product since it is removed from syngas at market specifications. Inventories n.4 and n.6 are identical since they describe crude methanol production. The purpose of this redundancy is to have separated bio-methanol and bio-DME synthesis pathways. The recycled hydrogen in crude methanol production is a secondary product that could be potentially exploited for other processes. The same hypothesis is approached in inventory n.6. Inventory n.7 describes the DME

synthesis from purified methanol. Steam and water are an input of this system since they represent distillation column consumption. Emissions for metallic catalysts were not considered in the overall assessment. The impact assessment of the three technologies was then evaluated with the Environmental Footprint (EF) method 3.0 to be able to analyse several factors such as climate change, land factor, human toxicity, ecotoxicity, freshwater, and resource use.

2.3. AHP methodology

The analytic hierarchy process method was employed in this study to determine the optimal alternative for biogas utilization. The AHP algorithm was implemented in MATLAB 2019b with the below-mentioned method. When performing the analysis, several factors were taken into account, such as (i) Climate change, (ii) Ecotoxicity, (iii) Human toxicity, (iv) Land use, (v) Water use, and (vi) Revenues. The reason why these categories were selected is that they involve environmental, economic, and social concerns with the final purpose of identifying the process with the best overall performance.

Environmental and social factors are the output of the LCA assessment, while economic ones are retrieved from the work of Negri et al. (2022) (Negri et al., 2022) where the economic assessments of different biogas utilization were evaluated. The work is based on the evaluation of CAPital EXpenditure (CAPEX)-OPERational EXpenditure (OPEX) analysis to assess the perspective revenues of the different production starting from the same capacity biogas plant. 1.9 M€/yr, 3.3 M€/yr, and 3.54 M€/yr are the expected technologies income for CHP, DME, and methanol, respectively.

Human toxicity is computed as the sum of factors such as carcinogenic and not. Pairwise comparisons and priority vectors are computed once the alternatives, criteria, and goals are selected. The alternatives are the three evaluated technologies, while the criteria are the LCA mentioned above categories. The pairwise comparison matrix (Eq. (15)) represents ratio scales between the weight of one criterion in i th row over another in j th column. The priority vector is then computed through the eigenvector method (Moghaddam and Hazlett, 2023). In AHP methodology, the comparisons are made using a scale that reflects the perceived importance, usually with values like 1, 3, 5, 7, and 9. When the assigned value is 1, the criteria have the same weight in the analysis while the element with a value of 9 is considered extremely more important than the others element being compared (Morsali, 2017).

$$Z = \begin{bmatrix} \frac{w_1}{w_1} & \dots & \frac{w_1}{w_n} \\ \frac{w_1}{w_1} & \dots & \frac{w_1}{w_n} \\ \vdots & \ddots & \vdots \\ \frac{w_n}{w_1} & \dots & \frac{w_n}{w_n} \\ \frac{w_n}{w_1} & \dots & \frac{w_n}{w_n} \end{bmatrix} \quad (15)$$

A matrix of the alternative criteria can be generated. Notably, the values of this matrix are the ratio between the different biogas utilization in a specific category. Eq. (16) shows an example of a climate change matrix:

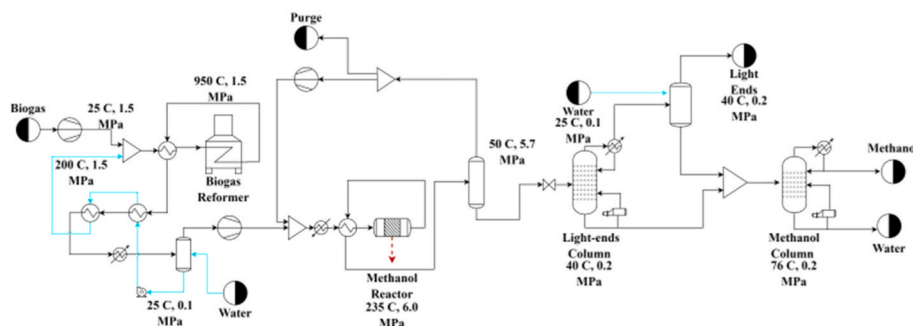


Fig. 4. Simplified flowsheet of methanol production from biogas.

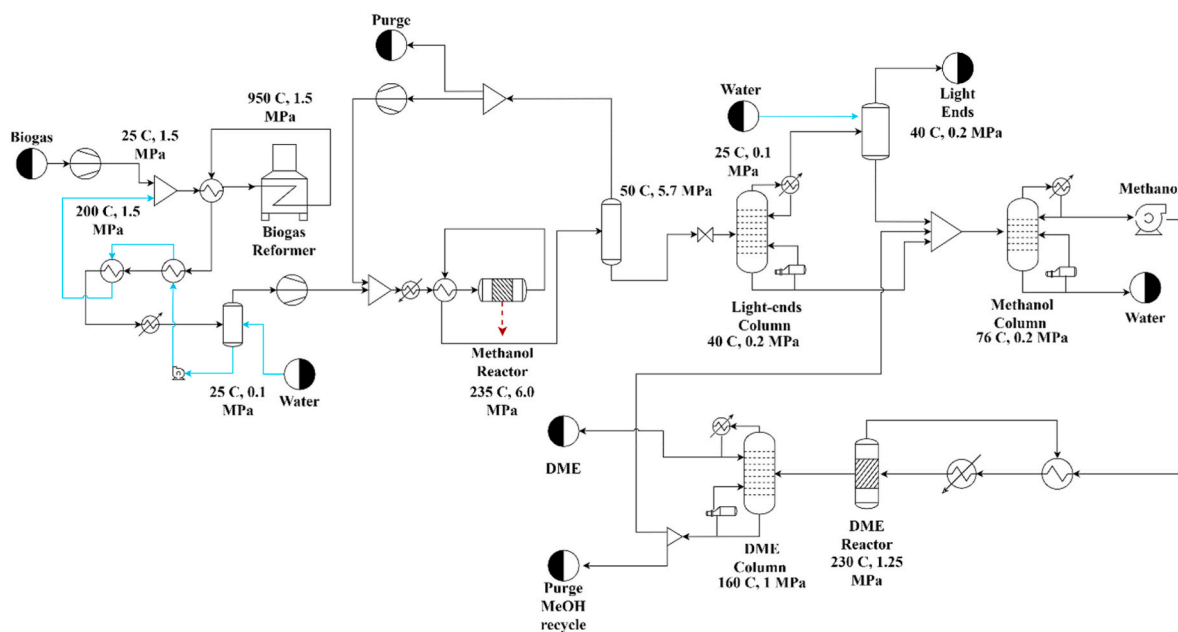


Fig. 5. Simplified flowsheet of DME production from biogas.

Table 1
List of inventories for LCA assessment.

Inventory n.	Description	Technology
1	Biogas purification	Biomethanol; Bio-DME; CHP
2	Bio-syngas production	Biomethanol; Bio-DME
3	Bio-syngas conditioning	Biomethanol; Bio-DME
4	Crude biomethanol production	Biomethanol
5	Biomethanol purification	Biomethanol
6	Biomethanol production for bio-DME	Bio-DME
7	Methanol purification and Raw bio-DME production	Bio-DME
8	Bio-DME purification	Bio-DME
9	Electricity production with CHP	CHP

$$Climate\ change = \begin{bmatrix} a_1 & a_1 & a_1 \\ a_1 & a_2 & a_3 \\ a_2 & a_2 & a_2 \\ a_1 & a_2 & a_3 \\ a_3 & a_3 & a_3 \\ a_1 & a_2 & a_3 \end{bmatrix} \quad (16)$$

where a_1, a_2, a_3 are the numerical input of climate change for CHP, DME, and methanol from biogas, respectively. Appendix Table A.10 shows the input value of the different matrices for each category.

The first run of the AHP method was performed with the same weight for each criterion, specifically 16.66%. In this way, the analysis is not influenced by external factors. The priorities weight may change depending on the evaluators, e.g. a company prioritizes economic benefit over climate change factors. In this work, the final aim is to have an absolute overlook without external bias. However, six (6) case studies are generated to evaluate the different alternatives when the criteria weights are modified. Table 2 describes the relative criteria weight for each case study. The last step is the computation of the relative percentage of the priorities by alternatives. In the end, the process with the best overall score is selected as favoured.

Fig. 6 describes the AHP decision tree to identify the optimal biogas utilizations.

Table 2
Criteria weight for the analysed case studies with AHP method.

Case study	Climate change	Ecotoxicity	Human toxicity	Land use	Revenues	Water use
1	16.67%	16.67%	16.67%	16.67%	16.67%	16.67%
2	40,91%	4,55%	4,55%	4,55%	40,91%	4,55%
3	7,14%	7,14%	7,14%	7,14%	64,3%	7,14%
4	45,1%	7,84%	7,84%	7,84%	23,53%	7,84%
5	19,5%	19,5%	19,5%	19,5%	2,52%	19,5%
6	2,63%	23,68%	23,68%	23,68%	2,63%	23,68%

3. Result and discussion

The three investigated processes have different outputs. The CHP cycle generates electricity and heat, while the others produce DME, and methanol as better described in Table 3.

The two chemical syntheses are analysed thanks to the evaluation of biogas molar conversion, H_2 molar conversion and chemical yield. Table 4 shows the main key performance indicators of the DME/methanol synthesis, including the design of the distillation columns. These performance indicators are not shown for biogas cogeneration since neither reactions nor purification steps are present. The computed conversion of methane in the reforming unit is 93% for both processes due to the same layout. This value shows good compliance with the literature data (Chen et al., 2019). The conversion of hydrogen as well is the same for both processes since the two technologies share the same methanol reactor.

In DME production, methanol is further converted in DME with a conversion of 89%. Although this value was obtained as a result of thermodynamic equilibrium instead of a proper kinetic model, it is still coherent with literature works assessing methanol conversion to DME on silica or zeolite catalysts. Moghaddam and Hazlett, for instance, observed a 87% methanol conversion when using ZSM-5 catalyst with a Weight Hourly Space Velocity (WHSV) of $0.5 \text{ g}_{MeOH}/\text{g}_{catalyst}$ catalyst (Moghaddam and Hazlett, 2023).

A further scope of this research work is to analyse the potential of the system without accounting for the design of the reactor unit. The value of 33% for CO_x conversion is a good result describing how these chemical pathways convert CO_2 to advanced chemicals. The adopted Gibbs reactor for DME production is leading to a single-pass DME yield

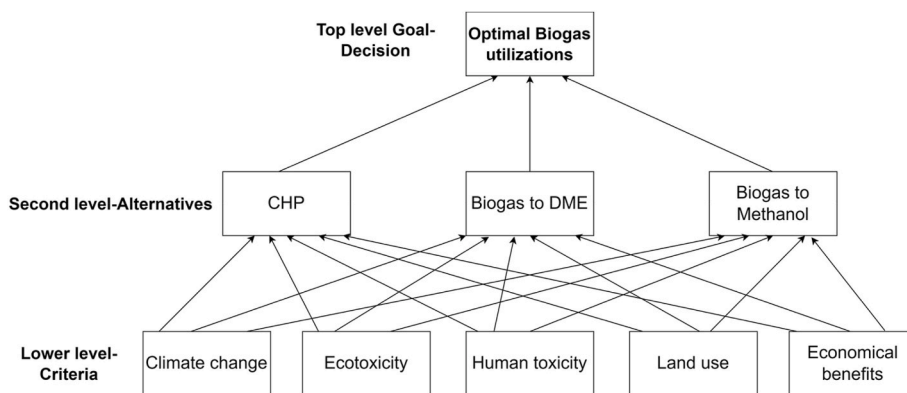


Fig. 6. AHP decision tree.

Table 3

Main input and output of the three technologies.

Technologies	Input	Output
CHP	500 Nm ³ /h	860.0 kWh of electricity 1472.2 kWh of heat
Biogas to DME	500 Nm ³ /h	333.3 kg/h of DME
Biogas to methanol	500 Nm ³ /h	450.5 kg/h of methanol AA

Table 4

Main key performance indicators of methanol and DME synthesis.

Chemicals	DME	Methanol
Biogas reforming		
χ_{CH_4}	92,8%	92,8%
Chemical synthesis		
χ_{H_2} per pass	20,7%	20,7%
χ_{CO_x} per pass	32,6%	32,6%
$\chi_{Methanol}$ per pass	88,6%	-
Purification section		
DME column	5 trays Reflux Ratio 1.5	-
Methanol column	-	35 trays Reflux Ratio 1.5

overestimation, affecting the LCA implementation. However, a lack of kinetic implementation is reported in the literature for DME synthesis.

Even if process simulation performances are not the main point of

this work, they are nevertheless required to assess and compare the environmental footprint of the three technologies.

The cradle-to-gate diagrams of the biogas utilizations are attached in the Appendix section. Several impact categories are analysed for each technology and the obtained results are expressed with Point (Pt) as a unit of measure in compliance with SimaPro software unit to display the resulting impact. The Pt unit is defined as a dimensionless value in the environmental indicator method that represents one thousand of the one-year environmental burden experienced by the average European population (Morsali, 2017). Sixteen vectors with a length equal to 3 are generated and each of them represents an LCA category. The size equal to 3 is due to the three evaluated processes. The data are normalised concerning absolute maximum value to compare the technologies.

Fig. 7 depicts the LCA comparison assessment. The values for human toxicity, ecotoxicity, land use, and water use are similar among the three technologies. The negative value of CHP layout proves not only that it contributes less to global warming potential (GWP) than DME and methanol production, but that, on the contrary it has a beneficial effect on the environment. Steam production and electricity intake from the national grid in the chemical pathways lead to increased climate change factor since both resources are generated from fossil fuels increasing the carbon footprint. Even though CHP technology releases a discrete quantity of CO₂ emissions during biogas combustion (1.72 kgCO₂/m³biogas), the other two technologies exploit energy-intensive units such as distillation columns, compressors, and reactors. The fact that several categories are negative for the three technologies is a perspective result for biogas utilization. The sum of this point for each category gives

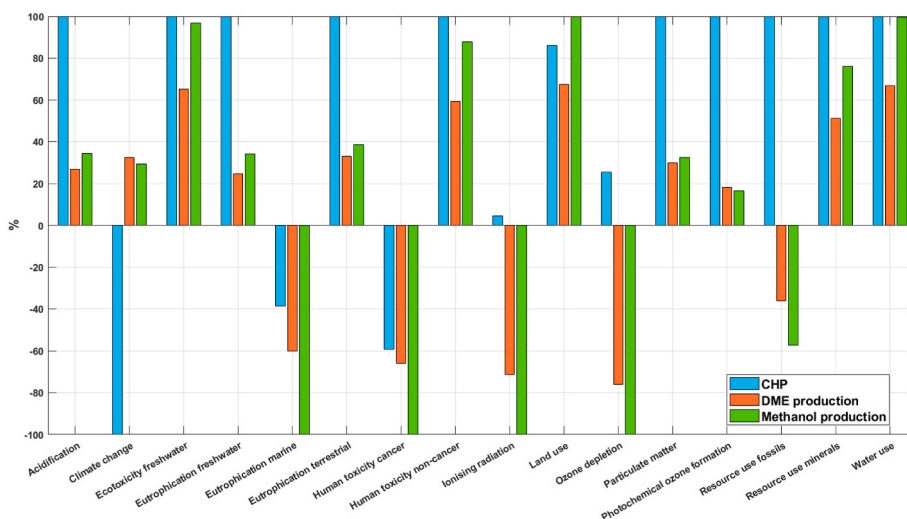


Fig. 7. LCA comparison assessment.

an idea of the overall environmental load of the processes. In particular, the overall best performance is noticed for DME production with a value of 235 μ Pt against 363 and 345 for cogeneration and methanol synthesis, respectively.

However, in order to compare the processes with the data available in literature, the real impact of the single category needs to be expressed with the appropriate unit of measure, i.e., climate change is described in $\text{kgCO}_{2\text{eq}}$. For this purpose, Table 5 shows the value of the different categories without normalization for all biogas uses. In their work, Barati et al. (2023) evaluated the environmental impact assessment of electrified CO_2 to methanol process. The global warming value reported for this analysis is equal to 2 $\text{kgCO}_{2\text{eq}}$, i.e. more than the LCA outcome of this research (Barati et al., 2023). As concerns DME, Karittha Im-orb et al. (2023) showed a total GWP of about 1.2 $\text{kgCO}_{2\text{eq}}$ to produce bio-DME via biomass gasification (Im-orb and Piroonlerkgul, 2023). The main difference with the proposed work can be identified in the presence of an amine scrubbing section, which accounts for 33% of the overall emission. Moreover, amine scrubbing systems are more energy-intensive for solvent regeneration than caustic ones (Zahedi et al., 2022). Alengebaway et al. (2022) reported similar value in

Table 5
Values of the different LCA categories for each technology.

Impact category	Unit	CHP	DME	Methanol
Climate change	kg CO2 eq	-5.57E-01	1.81E-01	1.64E-01
Ozone depletion	kg CFC11 eq	1.99E-08	-5.98E-08	-7.86E-08
Ionising radiation	kBq U-235 eq	2.11E-03	-3.34E-02	-4.67E-02
Photochemical ozone formation	kg NMVOC eq	2.01E-03	3.65E-04	3.29E-04
Particulate matter	disease inc.	2.59E-08	7.74E-09	8.40E-09
Human toxicity, non-cancer	CTUh	3.73E-08	2.21E-08	3.28E-08
Human toxicity, cancer	CTUh	-3.37E-10	-3.74E-10	-5.67E-10
Acidification	mol H+ eq	4.30E-03	1.16E-03	1.48E-03
Eutrophication, freshwater	kg P eq	2.02E-04	5.00E-05	6.93E-05
Eutrophication, marine	kg N eq	-3.18E-04	-4.97E-04	-8.26E-04
Eutrophication, terrestrial	mol N eq	8.99E-03	2.96E-03	3.48E-03
Ecotoxicity, freshwater	CTUe	2.37E+02	1.54E+02	2.29E+02
Land use	Pt	+1.55E+01	+1.21E+01	+1.80E+01
Water use	m3 depriv.	3.14E+01	2.10E+01	3.13E+01
Resource use, fossils	MJ	7.58E+00	-2.74E+00	-4.35E+00
Resource use, minerals and metals	kg Sb eq	9.20E-06	4.70E-06	7.00E-06
Climate change - Fossil	kg CO2 eq	-9.33E-01	-4.85E-02	-1.78E-01
Climate change - Biogenic	kg CO2 eq	3.74E-01	2.29E-01	3.41E-01
Climate change - Land use and LU change	kg CO2 eq	1.21E-03	6.52E-04	9.66E-04
Human toxicity, non-cancer - organics	CTUh	8.14E-10	3.76E-10	5.58E-10
Human toxicity, non-cancer - inorganics	CTUh	2.17E-08	1.35E-08	2.01E-08
Human toxicity, non-cancer - metals	CTUh	1.48E-08	8.16E-09	1.21E-08
Human toxicity, cancer - organics	CTUh	-6.89E-11	-1.15E-10	-1.76E-10
Human toxicity, cancer - metals	CTUh	-2.68E-10	-2.59E-10	-3.91E-10
Ecotoxicity, freshwater - organics	CTUe	7.63E-02	-5.68E-03	3.87E-02
Ecotoxicity, freshwater - inorganics	CTUe	3.16E+01	2.08E+01	3.10E+01
Ecotoxicity, freshwater - metals	CTUe	2.05E+02	1.33E+02	1.98E+02

different LCA categories for CHP technology. GWP impact in their work is 0.30 $\text{kgCO}_{2\text{eq}}$ against 0.55 $\text{kgCO}_{2\text{eq}}$ of the one computed in this analysis. This difference can be explained by considering the introduction of avoided products such as bio-fertilizers, which help to decrease the impact of this category. Finally, eutrophication potential (EP) categories in the two analyses are identical with values of 2.16×10^{-4} vs. 2.20×10^{-4} kg P_{eq} (Alengebaway et al., 2022).

As previously mentioned, the selected categories for the AHP methodology are climate change, ecotoxicity, human toxicity, land use, and economic benefits. The data were normalised for each section to guarantee the correctness of the analysis. Although a negative value in the LCA result, e.g., CHP climate change, can be considered good, when it is inserted in the AHP matrix it will result in the worst value. Whether needed, a logarithmic transformation was performed to overcome this problem. The matrix for each category is then generated and the output of the AHP method is the priorities by alternative, giving an idea of which process has the higher weight considering all the categories.

Fig. 8 depicts the AHP results highlighting the utilizations' weight for each type reported as a percentage value. The best alternative for climate change can be identified for CHP technology. Biogas to DME outperforms ecotoxicity, land use, human toxicity, and water usage better while methanol production has the most significant weight for revenues, i.e., economic benefit. Typically, the DME market value is higher than the methanol one, but this work considers the production normalised to 1 m^3 of biogas. Moreover, the methanol productivity is higher than the DME. The best process is assessed by the overall sum of the weight for each priority and, when the weight criteria are equal, DME production has the best overall score, with a result of 38.82%. However, the results of CHP and methanol products are close to it at 31.25% and 29.92%, respectively. DME production exhibits a stronger positive deviation than the other two technologies when no criterion has a priority.

After the first run, the other five (5) case studies are considered, and the obtained results are shown in Fig. 9 for each of them. Case study n.1 refers to equal criteria weight as discussed in the previous paragraph. In case study n.2, climate change and revenues have the highest weight, and CHP technology seems to have the best overall performance with an alternative weight close to 35%. DME and methanol production perform better when the priority is given to economic factors only (case study n.3). This can be easily explained by the fact that methanol and DME have a higher market value than electricity. In the fourth case study, climate change and revenues have the highest criteria weight, with a value of 45.1% and 23.5%, respectively. Moreover, CHP technology has the higher overall alternative weight than DME production (37% vs. 33%).

A weight priority of 42% for DME production is found when the categories are all equal, except for low impact for revenues (case study n.5). In the last case study, climate change and economic performances exhibit an impact lower than the others. In addition, DME production outperforms much better, with an overall score of 42% against 28% and 30% of CHP and methanol, respectively.

The outcome of this research highlights the importance of considering multiple factors when evaluating biogas utilization processes. Informed decision-making can drive the development and implementation of sustainable and efficient biogas utilization technologies, contributing to a greener and more sustainable energy future. The criteria for the evaluated case studies are selected to cover different scenarios. However, the analysis tool could be exploited in many situations depending on the decision-making criteria.

4. Conclusions

Performance, environmental impacts, and suitability of three biogas utilization processes, namely CHP cycle, DME production, and methanol production, were successfully compare in this research study. The analysis proved high methane molar conversion rates of 92.8% for both

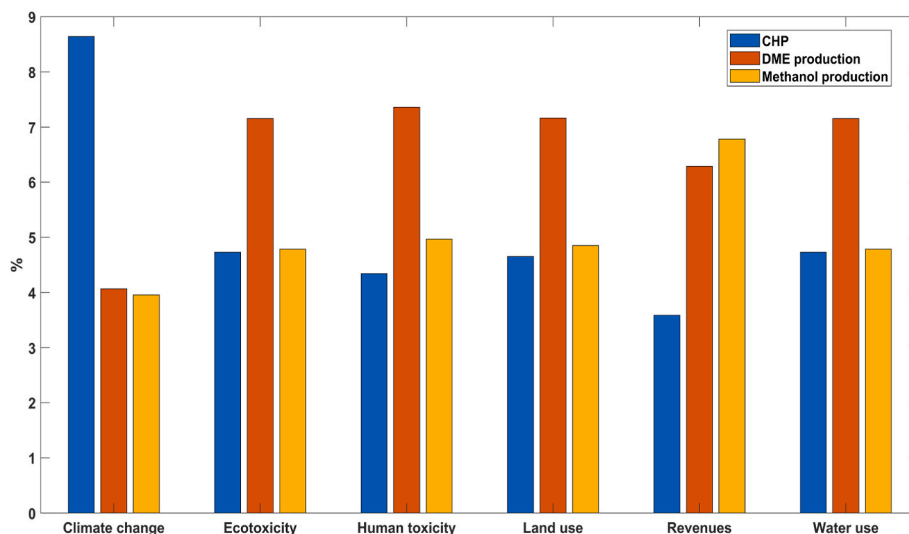


Fig. 8. AHP results by priorities.

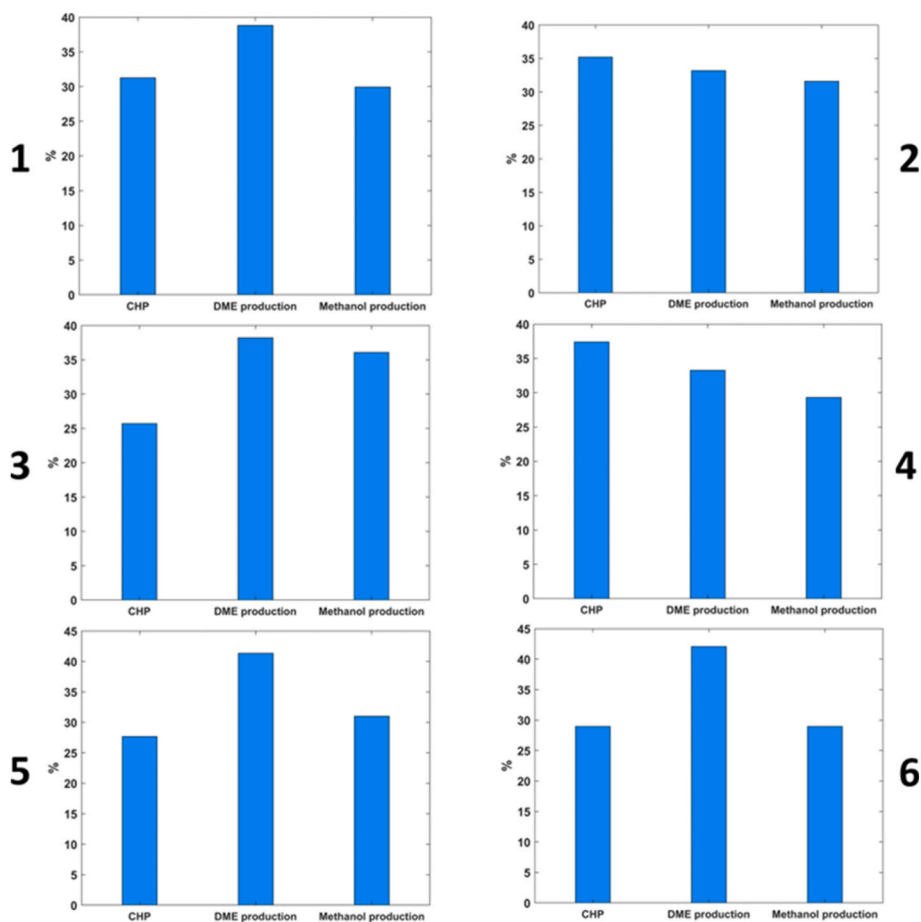


Fig. 9. AHP results for each case studies.

DME and methanol processes. Furthermore, DME production achieved a considerable methanol molar conversion rate equal to 86%. The chemical pathways exhibited significant CO_x conversion rates of 32.6%, remarking their potential as viable routes to convert CO₂ into advanced chemicals.

The life cycle assessment showed that CHP had the lowest global warming potential (GWP). At the same time, DME and methanol

production processes were influenced by steam production and electricity intake from the national grid, increasing their carbon footprints. The analytic hierarchy process analysis identified DME production with the highest overall weight, proving its better performance with regards to environmental impact categories such as ecotoxicity, land use, and water usage while methanol production showed the highest weight in economic benefits. Equal weight is given to each priority to avoid

external bias from the different needs of industry, politics, or society. A common pattern of the considered case studies can be detected in the best overall performance of CHP or DME production. According to the outcome of this study, between DME and methanol production, the first alternative results to be better.

In conclusion, this study contributes to the scientific understanding of biogas utilization processes and provides insights for policymakers, researchers, and industry stakeholders. DME production emerges as a promising option, balancing environmental performance and economic viability. However, choosing the most suitable process depends on specific contextual factors and priorities.

It is also worth remarking that this research work compares existing technologies and potential new ones, such as DME and methanol production from biogas, when no systematic heat integration is performed for the examined process configurations. In fact, including heat optimization in the work would be difficult since all the evaluated output could be strongly modified and unbalanced incorrectly. Furthermore, heat integration is considered a perspective work to perform the same analysis in further optimized technologies. Thus, it is an interesting improvement for those categories where utilities such as steam, water, and electricity have a huge impact on the results.

One of the possible future perspectives of this work could be the implementation of a robust kinetic model describing methanol dehydration in order to compensate the lack of process simulation and

kinetics for these systems in the available literature. This is also the reason why the authors have chosen to estimate DME production through the minimization of the Gibbs energy. The obtained conversion (87%) is clearly at an equilibrium state, i.e. a condition where the final production is overestimated. However, several experimental results, with different types of catalysts, in the literature report methanol conversion within the range of 80–85% (Vishwanathan et al., 2004; Keshavarz et al., 2011; Shahbeig et al., 2022). Finally, the reactor design and sizing are strongly affected by this thermodynamic evaluation. Indeed, very large volumes and long residence times are required to achieve the above-mentioned performance even though, this major concern slightly affects the LCA outcomes as emerged with the literature comparison.

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.

Data availability

Data will be made available on request.

Appendix A

Table A 1
Overall Input and Output for inventory n.1

INPUT		
Biogas, from grass {CH}-biogas production from grass-Cut,off, S	1	m ³
Water, decarbonised {RoW}-market for water, decarbonised-Cut-off, S	0.04	kg
Sodium hydroxide, without water, in 50% solution state {RER}- Cut-off, S	0.0199	kg
Electricity, medium voltage {IT}— market for — Cut-off, S	0.0004	kWh
OUTPUT		
Clean Biogas	1	m ³
NPK (15-15-15) fertiliser {RoW}-NPK fertiliser production-Cut-off, S	0.548	kg
Hydrogen sulfide	0.00008	kg
Wastewater, unpolluted {RoW}— market for wastewater, unpolluted — Cut-off, S	0.81	m ³

Table A 2
Overall Input and Output for inventory n.2

INPUT		
Water, deionised {Europe without Switzerland}-water production, deionised- Cut-off, S	0.238	kg
Clean Biogas	0.68	m ³
Electricity, medium voltage {IT}-electricity voltage transformation-Cut-off, S	0.069	kWh
Heat, district or industrial, natural gas {CH}-market for heat-Cut-off, S	7.19	MJ
OUTPUT		
Bio-Syngas	1	kg

Table A 3
Overall Input and Output for inventory n.3

INPUT		
Water, completely softened {RoW}-market for water, completely softened-Cut-off, S	2.01	kg
Bio-Syngas	1.18	kg
Electricity, medium voltage {IT}- market for -Cut-off, S	0.22	kWh
Heat, district or industrial, natural gas {CH}-market for heat-Cut-off, S	7.19	MJ
OUTPUT		
Clean Syngas	1	kg
Carbon dioxide, in chemical industry {GLO}— market for carbon dioxide— Cut-off, S	0.18	kg

Table A 4
Overall Input and Output for inventory n.4

INPUT		
Clean Syngas	1.13	kg
Electricity, medium voltage {IT}-market for-Cut-off, S	0.18	kWh
Steam, in chemical industry {RoW}-market for steam, in chemical industry -Cut-off, S	0.08	kg
OUTPUT		
Crude Methanol	1	kg
Hydrogen, gaseous {RoW}- hydrogen production, gaseous, petroleum refinery operation -Cut-off, S	0.006	kg

Table A 5
Overall Input and Output for inventory n.5

INPUT		
Crude Methanol	1.23	kg
Water, decarbonised {RoW}-water production, decarbonised-Cut-off, S	1.44	kg
Steam, in chemical industry {RoW}- production -Cut-off, S	0.68	kg
OUTPUT		
Pure Methanol	1	kg
Wastewater, unpolluted, from residence {RoW}-market for wastewater, unpolluted-Cut-off, S	0.00008	m ³

Table A 6
Overall Input and Output for inventory n.6

INPUT		
Electricity, medium voltage {IT}-market for-Cut-off, S	0.18	kWh
Steam, in chemical industry {RoW}-production-Cut-off, S	0.08	kg
Clean Syngas	1.13	kg
OUTPUT		
Crude methanol to DME	1	kg
Hydrogen (reformer)	0.0065	kg

Table A 7
Overall Input and Output for inventory n.7

INPUT		
Crude methanol to DME	1.09	kg
Water, decarbonised, at user {GLO}-market for-Cut-off, S	0.006154	kg
Steam, in chemical industry {RoW}-market for steam, in chemical industry-Cut-off, S	0.2809	kg
Electricity, medium voltage {IT}-market for-Cut-off, S	0.0005	kWh
OUTPUT		
Raw DME	1	kg
Wastewater, unpolluted {RoW}-market for wastewater-Cut-off, S	0.41	kg

Table A 8
Overall Input and Output for inventory n.8

INPUT		
Raw DME	1.55	kg
Water, decarbonised, at user {GLO}-market for-Cut-off, S	2.94	kg
Steam, in chemical industry {RoW}-market for steam, in chemical industry-Cut-off, S	0.29	kg
OUTPUT		
Pure DME	1	kg

Table A 9
Overall Input and Output for inventory n.9

INPUT			
Clean Biogas	0.58		m ³
Air	4		kg
OUTPUT			
Electricity	1		kWh
Heat, central or small-scale, biomethane (Europe without Switzerland)- < 100 kW-Cut-off, S	6.16		MJ
Carbon dioxide	1		kg
Nitrogen oxides	0.0001		kg
Carbon monoxide	0.004		kg
Sulfur oxides, IT	0.0001		kg

Table A 10
Input for each alternative matrix with the relative operations. Variable x indicates the impact value of the different categories computed with LCA.

LCA input	a ₁	a ₂	a ₃	Method
Climate change	3.05	1.44	1.39	$\frac{1}{e^x}$
Ecotoxicity	0.002	0.003	0.002	$\frac{1}{x}$
Human toxicity	13461776.10	22856966.45	15397936.10	$\frac{1}{x}$
Land use	0.06	0.08	0.06	$\frac{1}{x}$
Revenues	1.90	3.30	3.54	x
Water use	0.03	0.05	0.03	$\frac{1}{x}$

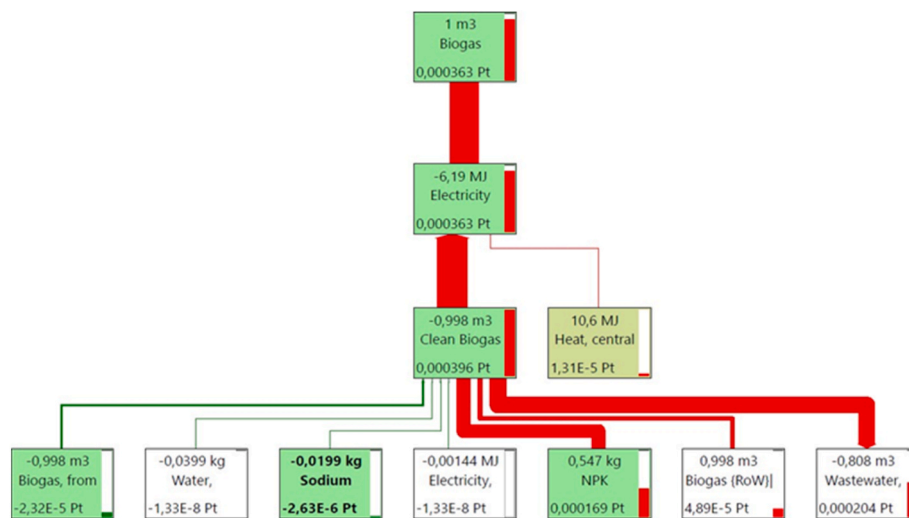


Fig. A.10. LCA network for the CHP technology.

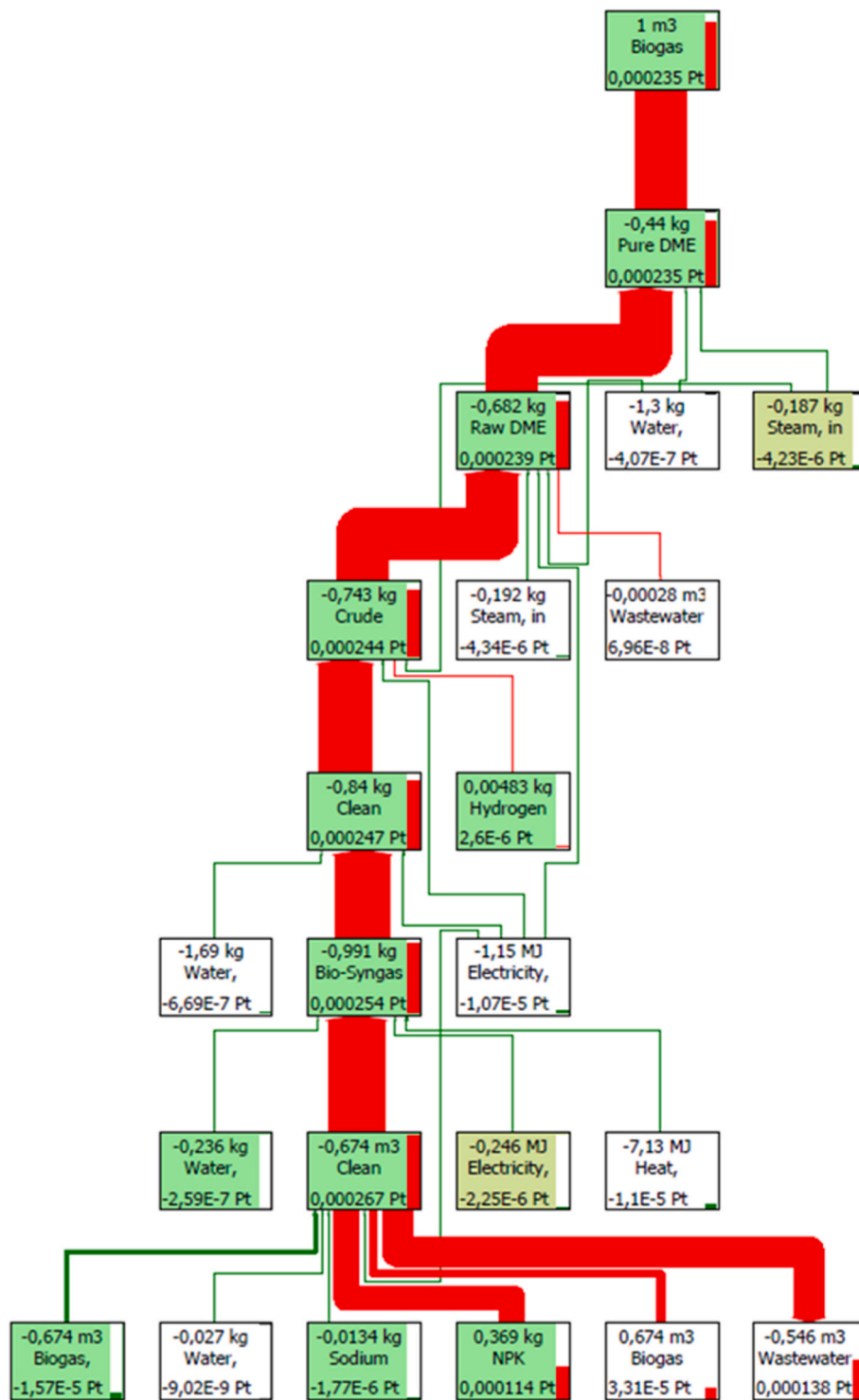


Fig. A.11. LCA network for the DME production from biogas.

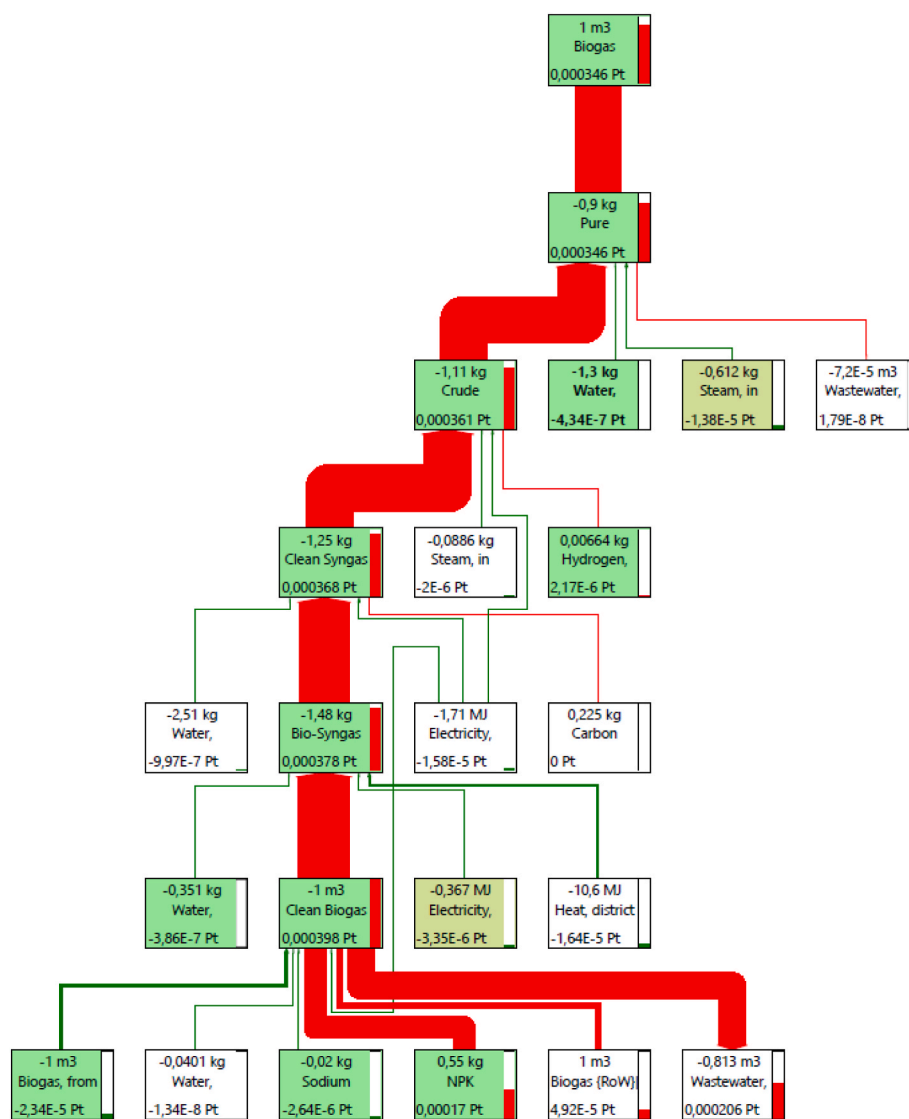


Fig. A.12. LCA network for the methanol production from biogas.

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