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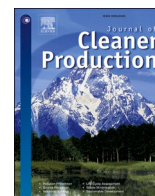
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Process design and downstream optimization of the direct synthesis route for cleaner production of dimethyl ether from biogas

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ABSTRACT

This study investigates an innovative method to produce dimethyl ether (DME) by direct synthesis from syngas derived from biogas. The proposed process was rigorously simulated in Aspen Plus, highlighting the main sections: (i) biogas tri-reforming, (ii) dimethyl-ether synthesis, and (iii) DME purification. The tri-reforming section has a CO₂ and CH₄ conversion of 27.3% and 96.2%, respectively. A novel catalyst suitable for CO₂-rich feed was chosen for the DME production to allow 60% conversion of CO₂. Product separation is achieved via several absorption and distillation columns, ensuring that the operating conditions are kept mild to avoid expensive refrigeration. An optimization analysis was performed to identify the most suitable layout of the downstream process. This was identified through the evaluation of performance indicators such as utility usage and operating expenses. A wide range of purification strategies have been evaluated, and two scenarios are proposed based on the results. Configuration A produces 5.34 ktpy DME and 1.26 ktpy methanol, while Configuration B produces exclusively 6.21 ktpy DME. The process configurations were analysed by means of key techno-economic indicators and sustainability metrics. Both processes have an energy intensity of 14.5 kWh/kg. The reforming unit has a negligible footprint as it is thermally sustained from biogas combustion, but the reboilers are the main contributors for plant CO₂ emissions. Configuration B has the best economic value with 11,634 k€ of NPV after 25 years and a payback time of 4 years.

1. Introduction

Carbon dioxide emissions represent a worldwide problem, as human factors strongly affect the increase of CO₂ concentration in the air (Climate.gov, 2021). To mitigate this, the Paris Agreement by UNFCCC (United Nations Framework Convention on Climate Change) limits global warming to below 2 °C, compared to pre-industrial levels (UNFCCC, 2016). In this context, the European Renewable Energy – Recast to 2030 (RED II) has the target to switch fossil fuel into biofuel reaching a share in the transportation sector of at least 3.5% in 2030. Biogas is identified as an important contributor to the production of advanced biofuels in the RED II sustainability criteria (European Commission, 2020).

Biogas mixture typically contains about 50–70% methane (CH₄), 30–50% carbon dioxide (CO₂), and other trace impurities (Magomnang et al., 2014). It is produced via anaerobic digestion (AD) of organic

material such as agricultural wastes, manure, wastewater, and sludge (Scarlat et al., 2018). Biogas production benefits the economy, providing reasonably priced green energy. In 2020, 191 TWh of biogas were produced, accounting for 4.6% of the entire amount of gas consumed. Currently, Europe is producing 3 billion cubic meters (bcm) of biogas and biomethane, equaling Belgium's total gas demand. Europe will be able to produce 35 bcm by 2030, meeting 10% of the EU overall gas demand (EBA, 2021). Biogas is typically used as fuel in Combined Heat and Power (CHP) plants to generate heat and electricity. Nevertheless, the intrinsic amount of CO₂ in this technology is emitted into the atmosphere leading to non-zero overall carbon emissions (Furtado Amaral et al., 2020).

Alternative utilization considers biogas as feedstock for cleaner production of advanced chemicals. This technology is called Heat, Power, and Chemicals (HPC). HPC plants convert biogas into biobased products such as dimethyl ether (DME), methanol, and acetic acid. In

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this process, both CH₄ and CO₂ are chemically active. HPC has a carbon footprint 30% lower than conventional biogas exploitations, as shown through a Life Cycle Assessment (LCA) (Fedeli and Manenti, 2022a). Thus, this work focuses on the direct synthesis of bio-DME from biogas feedstock.

The utilization of DME as a clean fuel is well-considered for the replacement of conventional fuels such as diesel, which is the most relevant source for particulate matter and nitrogen oxides in urban centers and is completely banned from some European cities (Fedeli et al., 2022).

As suggested by Vakili et al. (2011) bio-DME combustion drastically decreases the emissions of pollutants such as hydrocarbons, CO, NO_x, and particulates. The latter are prevented since the DME molecule has a high oxygen content, i.e., 34,8% w/w, and no C–C bonds (Matzen and Demirel, 2016). The chemical analogies of DME with Liquefied Petroleum Gas (LPG) allow it to replace the latter in household cooking (Larson and Yang, 2004). Moreover, there are perspectives on using DME for the production of olefins and gasoline (Cordero-Lanzac et al., 2020). DME is industrially synthesized through single and two-step routes. DME is directly obtained from syngas in a single step, while the second one splits the process into methanol production and its further dehydration units (Azizi et al., 2014; Bildea et al., 2017). Fig. 1 shows the main differences between the two technologies.

Bi-functional catalysts are employed in the direct DME synthesis process. The metallic function catalyzes the CO_x hydrogenation, while the acidic function favours the methanol dehydration. These hybrid catalysts are obtained through the physical mixing of Methanol Synthesis Catalyst (MSC) and Methanol Dehydration Catalyst (MDC). Typically, mixtures of Cu/Zn/Al₂O₃ as MSC and γ -Al₂O₃ as MDC are mostly employed for this purpose (Gogate et al., 1991).

One-step synthesis has recently gained attention for its higher efficiency than indirect synthesis. This is due to two different factors: (i) hybrid catalysts employment partially increases the CO conversion (Vakili et al., 2011); (ii) no need for two reactors and intermediary purification steps led to process cost reductions. The main drawback of the single step concerns the design of the DME purification section due to the presence of unreacted syngas, methanol, and carbon dioxide. The conventional separation section for direct DME synthesis is represented in Fig. 2 (Azizi et al., 2014). DME purification strategies in the one-step synthesis are already present in the literature showing critical issues concerning this stage. Han et al. (2009) proposed a purification process for the single-step DME synthesis to reach high DME purity. However, the model feasibility is unclear as an economic analysis is not reported. Chen et al. (2013) proposed a different configuration to increase DME productivity through methanol recycling, but the process economic analysis is uncertain as the high impacting refrigeration costs are not included. (Merkouri et al., 2022) performed a techno-economic analysis

on direct DME synthesis from landfill gas. The results show proof of the current feasibility of CO₂ valorization process. Present and past research reveals a gap in demonstrating the environmental impact and the economic feasibility of direct DME synthesis. Another problem to overcome is the limitation of duty temperature below zero degrees. Mevawala et al. (2017) presented a plant-wide modelling of a direct DME synthesis where the DME purification column temperature reaches -20 °C. Considering the rural context of biogas processes, milder conditions are to be obtained. These problems and uncertainty in research strongly affect the commercialization of this technology.

This original study focuses on the direct DME synthesis from biogas and its purification steps to fuel-grade quality. Direct DME production from CO₂-rich feedstock (biogas) is an intriguing topic for several reasons: (i) GHG conversion into an advanced fuel has the potential to replace diesel utilization, (ii) process performance is better than the two-step route synthesis, (iii) the technology requires less space in terms of footprint. This paper presents the conceptual design and plant-wide model of the direct DME synthesis process. Each process section is investigated through economic and environmental analysis. The main objective is to determine the overall plant feasibility in terms of economic and environmental impacts. The process scale was selected according to the average capacity of a biogas farm (about 6 mln m³ biogas per year).

A biogas tri-reforming is modelled to enhance CO₂ conversion into bio-syngas. Biogas tri-reforming was analysed by Vita et al. (2014), while Zhang et al. (2015) integrated this technology with DME production showing its feasibility. De Falco et al. (2016) evaluated, with thermodynamic assessment, the dimethyl ether (DME) direct production from CO₂-rich feedstock to show the potentialities of using CO₂ as reagent in one-step DME synthesis. A thermodynamic threshold with a DME yield lower than 30% is present when the CO₂/CO ratio is greater than 2 in the feedstock.

A key novelty of this work is the modelling of the DME synthesis step with an innovative Cu/ZnO/ZrO₂-Ferrite catalyst that is suitable for CO₂ enriched feedstock (such as biogas) to overcome thermodynamic threshold and limitations in CO₂ conversion.

In addition, modern catalysts are kinetically modelled to optimize the DME synthesis in terms of CO₂ conversion. Next to conversion, the main challenge is the design of an effective downstream process that must focus on reducing OPEX and mitigating emissions caused by the use of refrigerants. Conventional refrigerants have an average Global Warming Potential (GWP) of 1000, while the GWP of water usage as a coolant medium is assumed to be negligible (Sanguri et al., 2021). In this respect, the condition to be respected is to employ only cooling water (by keeping the operating temperatures higher than 20 °C). This approach is followed in optimizing the DME downstream section.

Several works in literature proposed and studied the purification section in the framework of DME production. Ballinger and Ii (2017)

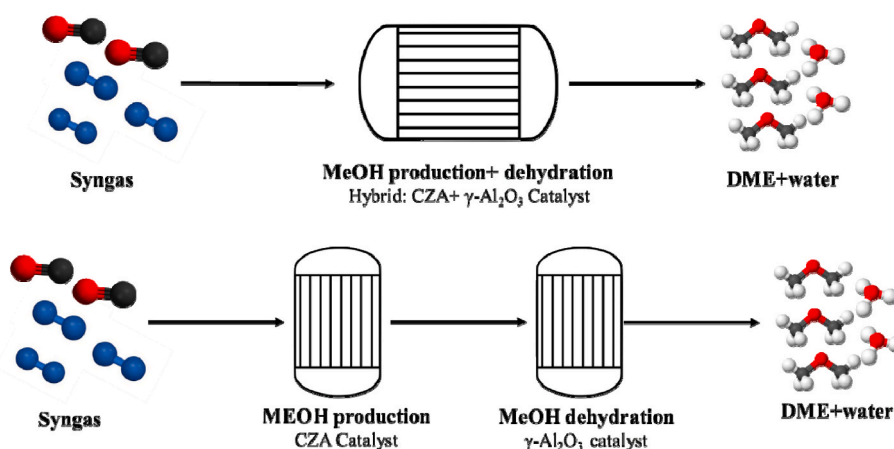


Fig. 1. Main differences between single and two-step DME synthesis routes.

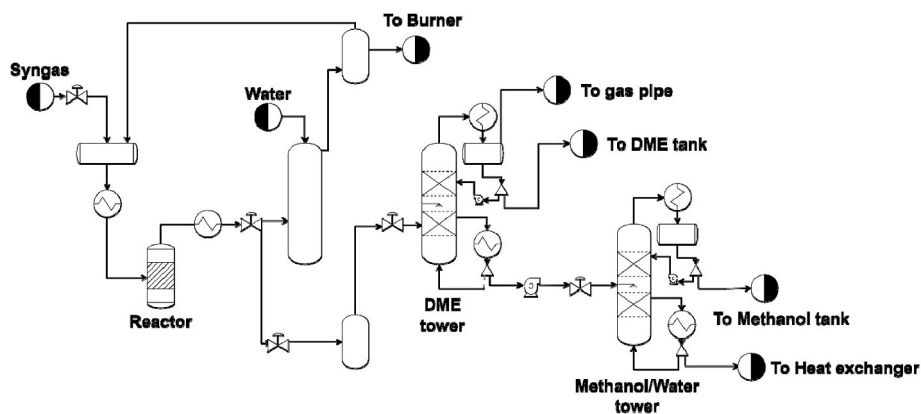


Fig. 2. Conventional DME purification steps in a single step process (Azizi et al., 2014).

designed a distillation system to purify DME focusing on size constraint for easy transportation, process intensification, and separation efficiency. Bildea et al. (2017) presented the optimal design of novel DME processes based on reactive distillation. The new configuration were optimized in terms of minimizing the total annual costs, leading to savings of 30% in CAPEX and 6% in energy requirement. This manuscript deals with the process optimization focusing on OPEX and the recovery ratio of valuable products.

The DME purification section was optimized by performing a multiple scenarios evaluation. This choice is due to downstream operations, which are the uncertain step of the proposed technology. As highlighted in the state of the art, few works in the literature discussed and analysed the DME downstream, its design optimization, and the economic evaluation. One of the aims of this work is the research of an optimal purification section in the context of a biogas production farm. Moreover, the configuration of DME reactor, the heat integrations, the separation, and its recycling is further discussed and proposed as an innovative configuration. Parameters such as conversion, recovery ratio, and yields evaluate the technical process performance. Sustainability metrics were used to assess the environmental intensity of the processes. Moreover, Payback time (PBT) analysis and Cash Flow Analysis (CFA) were carried out to assess the plant economic feasibility and compare the best two process configurations.

2. Methodology

The process for converting biogas into bio-DME was rigorously simulated in Aspen Plus v11. The kinetics of tri-reforming and DME synthesis are modelled in Aspen Plus as Langmuir Hinshelwood Hougen Watson (LHHW) reactions. The described equation is the following:

$$r = \frac{[Kinetic\ factor] \cdot [Driving\ force]}{[Adsorption]} \quad (1)$$

All the stream properties and relevant information are presented in the *Supplementary Information*. The process is split into three different sections: (i) biogas tri-reforming for syngas production, (ii) direct bio-DME synthesis, and (iii) DME purification step.

According to the chemicals present in the system and the operating conditions in the process, Redlich-Kwong-Soave (RKS) and Non-Random Two Liquid (NRTL) thermodynamic methods are selected as most suitable property models (Kontogeorgis and Folas, 2009). All the required parameters for these property methods are available in Aspen Plus v11.

Based on a decision tree optimization, two process configurations (A and B) are proposed as main case studies for optimizing the separation and purification steps. Fig. 3 illustrates the block flow diagrams of the two configurations.

The feedstock composition was retrieved through an analysis of biogas derived from silomais, an agricultural crop, within an anaerobic digester plant located in central Italy (Fedeli and Manenti, 2022b). Silomais serves as a dedicated energy crop, and significant fluctuations

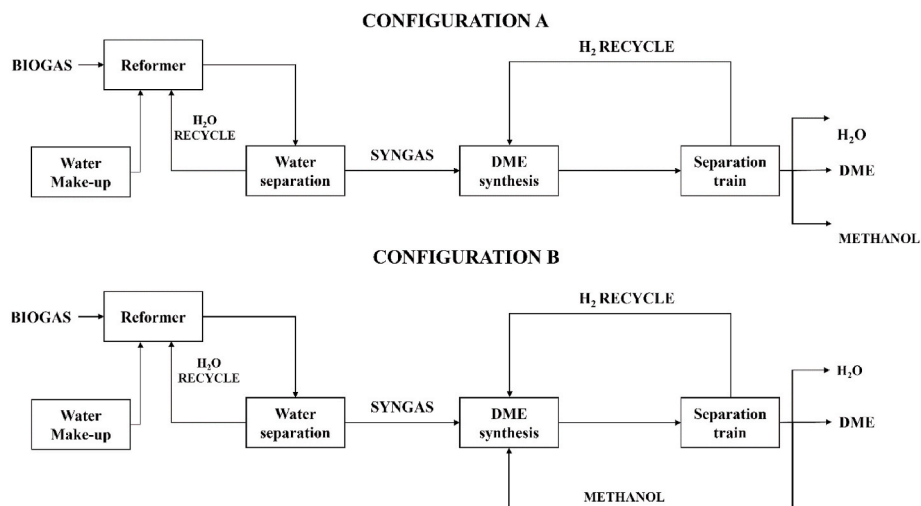
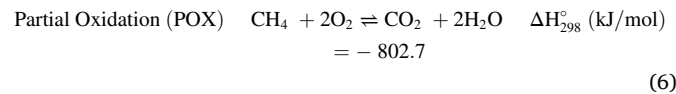
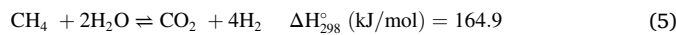
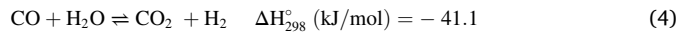
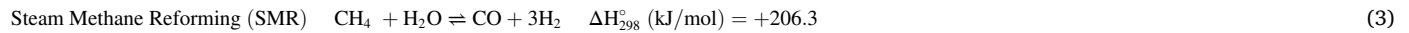
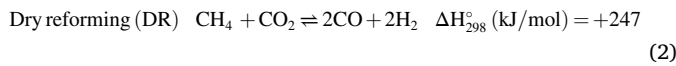


Fig. 3. Block Flow Diagrams of the configurations A and B.

in biogas composition are expected (Fuksa et al., 2020). The predominant impurities in the feedstock arise from sulfuric compounds, which are effectively mitigated by the installation of active carbon filters.

The biogas flowrate is taken from literature data considering a biogas plant with an Installed Electricity Capacity (IEC) of 1.2 MW_{el}. This value is greater than the average capacity in the European Union of 0.6 MW_{el}, significantly affected by the statistics of small countries such as Austria, Denmark, Estonia, and Switzerland (Report, 2018). The choice is done to evaluate the potentiality of DME production from biogas in countries where the biogas technology is well developed and established, i.e. UK with an average capacity of 2.68 MW_{el}.

All the process details required to build the rigorous process simulation are reported hereafter. Biogas enters the system and is compressed by a three-stage compressor (with intercooling) to 15 bar, i.e. the required conditions of a typical reforming process. This stream is heated and blended with recycled steam using a process-process heat exchanger to recover energy. The mixture is then fed into the tri-reformer unit. The reformer reactor is modelled as a multi-tubular Plug Flow Reactor (PFR). Pressure drops are estimated with the Ergun equation. The kinetic model is taken from the work of Balasubramanian et al. (2018) and includes the following chemical equations:



The detailed kinetic parameters are reported in the *Supplementary Information*. POX reaction is included in the model of the intrinsic oxygen content in the biogas. The validation of the kinetic model was

previously done in the work of the (Balasubramanian et al., 2018) with a reduced model, resulting in a R² of 0.9995 between simulated data and experimental ones.

The typical catalyst adopted by the industry is NiO–MgO–ZrO₂. A steam/methane ratio close to unity is chosen to favour the DR reaction, enhancing CO₂ conversion. The hydrogen yield in the tri-reformer unit is evaluated as follows:

$$Y_{\text{H}_2} = \frac{F_{\text{H}_2, \text{out}}}{2 \cdot F_{\text{CH}_4, \text{in}} + F_{\text{H}_2\text{O}, \text{in}}} \quad (7)$$

The combustion of fresh biogas and tail gases provides the thermal duty of the reformer. This configuration is evaluated to lower the CO₂ emission in this section. GHG emissions from biogas, and its products, are considered negligible in the overall environmental assessment since they are biogenic (EBA, 2020). The fresh biogas is taken from the same anaerobic digester considering an extra 15% capacity. A Heat Exchanger Network (HEN) is designed for the energy integration process. Thus, it is done by exploiting the high temperature of the reformer outlet with a series of thermal recoveries. The tri-reformer working temperature of 950 °C is set according to the literature review and conventional operations of tri-reforming unit (Pham et al., 2021).

This design aims to minimize the external duties of the process and its associated operational costs. Indeed, only heat exchanger (cooler) E-101 works with cooling water. The HEN is realized by coupling the

hot streams and the cold streams of the process flowsheet, as shown in Fig. 4. Syngas exits at 950 °C and has to be cooled down to 25 °C to separate excess water from syngas. It enters the first heat exchanger in the network (E-100) and exits at 692 °C. Heat is removed thanks to feeding stream 2, which pre-heats from 162 °C to 500 °C. The preheating temperature is the maximum temperature guaranteed by the HEN to vaporize the water in the recycle loop. Stream 4 proceeds to enter the ECO process-to-process heat exchangers. ECO stands for economizer and is the heat exchanger designed to bring water from a subcooled condition at 15 bar to the boiling point. This equipment is kept separate from the vaporizer (VAP) that is designed for the complete vaporization of the water stream. This unit guarantees the complete vaporization of the stream, avoiding the phenomena in other heat exchangers. In the

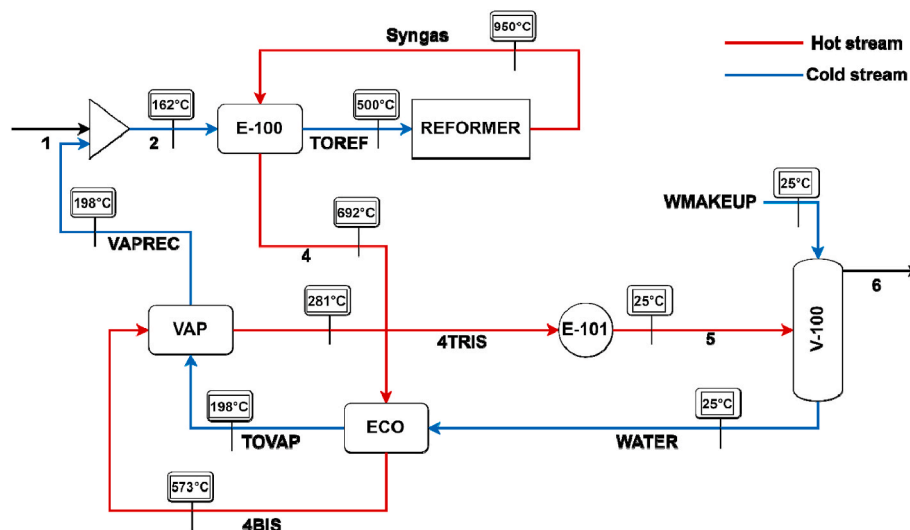


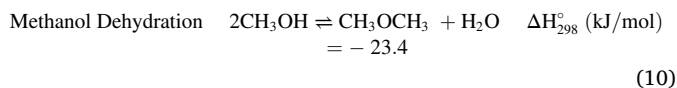
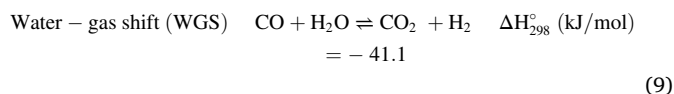
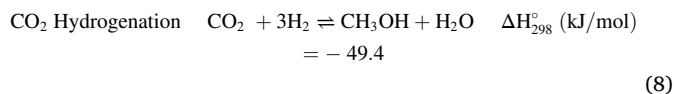
Fig. 4. Block Flow Diagram of the heat exchanger network (HEN).

economizer, stream 4 passes from 692 °C to 573 °C of stream 4BIS, while WATER stream passes from 25 °C to 198 °C. In the vaporizer, stream 4BIS passes from 573 °C of stream 4BIS to $T = 281$ °C of stream 4TRIS. It is visible that the water stream maintains the same temperature, indicating the passage of phase from liquid to vapor. Water is mixed with the biogas feed stream and the loop is closed.

Stream 4TRIS requires a temperature decrease for the further separation. Heat exchanger E-101 is cool down the temperature to 25 °C, thanks to the cooling water utility. Stream 5 is sent to a separation vessel V-100, where 22 kmol/h of makeup water at 14 bar and 25 °C (WMA-KEUP) is sent to integrate water consumed during reformer reaction in the WGS.

After the reformer section, syngas pressure is increased from 15 to 40 bar by means of a two-stage compressor (with intercooling step). Once the desired operating conditions are achieved, DME synthesis step can be performed. These process sections are the same for the two process configurations but slightly differ for the DME synthesis and further purification step. The DME reactor is modelled as a multi-tubular isothermal PFR. The Gas Hourly Space Velocity (GHSV) has values between 3000–10,000 h^{-1} depending on the recycle ratio implemented. The reactor space velocity value is chosen to be inside the standard range for DME synthesis (Maloney, 2007). Tubes are filled with bi-functional catalysts, as described by (Wild et al., 2022). Note that the Cu/ZnO/ZrO₂-Ferrite catalysts are more suitable for CO₂-rich feedstock than conventional ones (Wild et al., 2021). Aspen PLUS kinetic parameters of the catalyst are retrieved from the work of Wild et al. (2022). This kinetic model is validated in the previous work with a 5-fold cross-validation with a mean error of 5% for DME productivity.

The reaction set is described by the following chemical equations:



The selected reactor technology is a catalytical multi-tubular reactor with a preheating and a cooling section, known as RECS (Reactor, Evaporator, Condenser, and Separator). The fresh feeds enter the first section and are distributed in the tube bundle to be heated. The stream is heated up to the reaction temperature through a vapor-film condensation on the shell side. The tubes are empty in the preheating section to prevent any type of reaction. However, tubes are filled with catalysts in the cooling section to allow the DME synthesis. Boiler Feed Water (BFW) is used as a cooling medium in the shell. The heat released during reactions led to BFW evaporation and vapor production. Thus, it will condense in the preheating section. To model the RECS reactor, a PFR is

coupled with a series of heat exchangers. Fig. 5 shows the block flow diagrams of the reactor configuration. In this picture, RECS, E-RECS, and E-RECS1 represent the reactor where DME is produced, the cooling section, and the preheating step respectively. In the process simulation, these three units model the real unit RECS, which is a licensed technology of Politecnico di Milano.

L1COND and L1VAP are the material streams of the BFW cycle. L1COND flowrate is selected to guarantee an isothermal profile inside the reactor. L1VAP enters the process-process exchanger E-RECS1 to preheat the fresh feed (stream 9). The inlet temperature of the feed is regulated by an external heat exchanger to achieve L1VAP condensation. Reactor pressure drops were evaluated with the Ergun equation. The reactor products (RECSOUT) consist of unreacted syngas, DME, water, and methanol. Compound selectivity is computed through the following equation:

$$S_j = \frac{n \cdot (\dot{n}_{j,out} - n_{j,in})}{(\dot{n}_{CO_2,in} - n_{CO_2,out})} \quad (11)$$

where n is the number of carbon atom of j th molecule, and \dot{n} is the molar flowrate.

This mixture requires a purification step to obtain high-purity DME and methanol. ASTM D7901-14 standard specification is selected for DME purity grade, with a final composition higher than 98.5% w/w (Oguma, 2017). A decision tree optimiser was employed to design the purification step. The main constraint is to use cooling water and steam utilities only in order to achieve milder process conditions and avoid expensive refrigeration consumption, ultimately leading to a reduction in OPEX and GHG emissions. The key performance indicators (KPI) used to select the most appealing process configurations, are the Operational Expenditures (OPEX) and the DME recovery ratio (DME_{RR}) defined as:

$$DME_{RR} = 100 \times \frac{\text{Purified DME outlet} \left[\frac{\text{kg}}{\text{h}} \right]}{\text{Raw DME inlet} \left[\frac{\text{kg}}{\text{h}} \right]} \quad (12)$$

Multiple scenarios are evaluated introducing the unit step-by-step. The decision tree is shown in Fig. 6. The first step is useful to choose the unit after the DME reactor. Three different options are taken into consideration at level 1: (A₁) refrigerated vessel, (B₁) chilled vessel and absorption column, (C₁) absorption column. Among them, B₁ and C₁ show the best results in terms of OPEX and recovery ratio and are brought forward to the second step which focuses on the process design configuration after the absorption column. The three cases at level 2 are: (A₂) Partial condenser distillation column with a recycle of uncondensable gases, (B₂) Distillation column with partial condenser for DME extraction, (C₂) Absorption column. After this level, better KPIs were found for the configuration B₁. Case B₁-B₂ is dismissed as it showed the worst KPIs. Case B₁-A₂ is improved by selecting cooling water as utilities rather than refrigerants. Case B₁-C₂ has the best DME recovery ratio and no refrigeration duties. Nevertheless, water injection

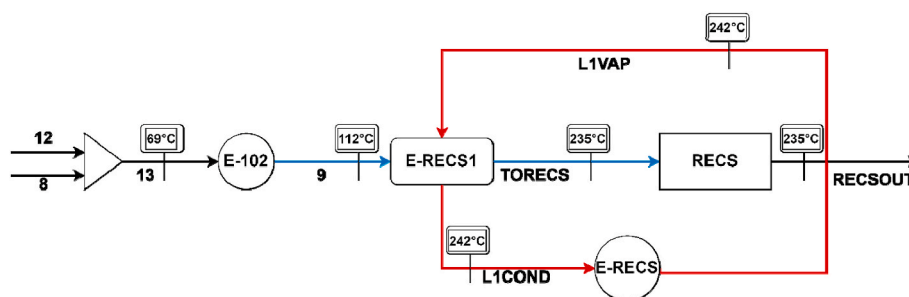


Fig. 5. Block flow diagram of the DME reactor.

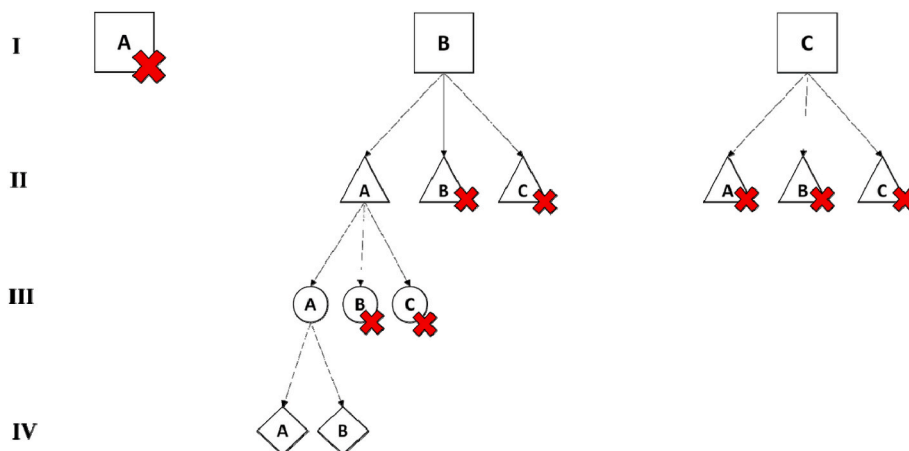


Fig. 6. Decision tree used in the analysis.

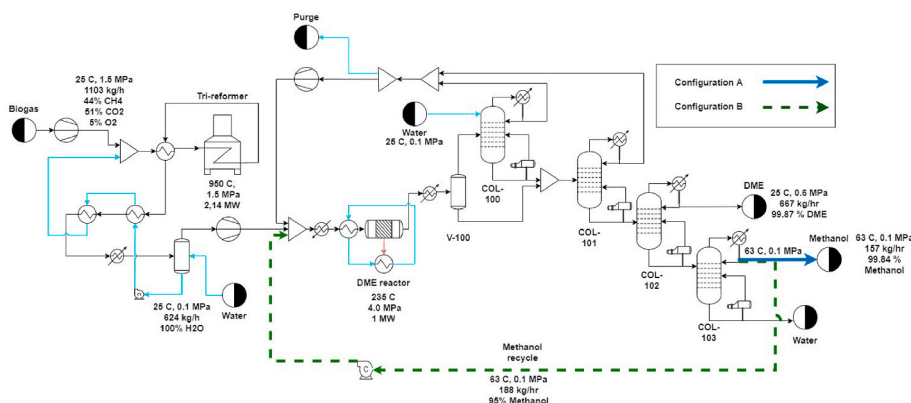


Fig. 7. Flowsheet of the process configurations A and B.

Table 1
List of Equipment of the DME purification step.

Code	Equipment	Description
V-101	Vessel	Remove uncondensable gases from DME, methanol, and water
C-100	Absorption column	Water absorption for DME, methanol, and water
C-101	Distillation column	Remove the CO ₂ from the liquid mixtures
C-102	Distillation column	Purify DME from methanol-water mixtures
C-103	Distillation column	Purify methanol from water
K-101	Compressor	Recompress the recycled syngas to DME reactor

in the absorption tower increases the OPEX of this scenario. Among the two scenarios (B₁-A₂, B₁-C₂), the latter is excluded for its poor feasibility. The third step focuses on the design of the DME distillation column. The distillation column configurations at level 3 are: (A₃) Partial condenser, (B₃) Partial condenser and side cut for methanol, and (C₃) Total condenser column. In this case, only the configuration B₁-A₂-C₃ provides a DME purification according to the ASTM D7901-14 standard. Then, this design is tested in two different ways, at decision level 4, using a: (A₄) Methanol production column, and (B₄) Methanol recycle column. The difference between them is the final scope of the produced methanol in DME reactor. The B₁-A₂-C₃-A₄ and B₁-A₂-C₃-B₄ represent the process configurations A and B, as shown in Fig. 7. Table 1 summarizes the equipment used in both configurations. Specific details regarding the equipment unit are provided in the next sections.

2.1. Environmental analysis

Biogas to bio-DME synthesis is well inserted in the circular economy

context, being a waste-to-product process (Baena-Moreno et al., 2021). Sustainability metrics are evaluated to assess the environmental impact of this process. The chosen indicators are material intensity (MI), environmental factor (E_F), energy intensity (EI), water consumption (WC), and CO₂ emissions (Schwarz et al., 2002). MI indicates the input materials used per unit of output. E_F indicates the specific waste produced in the process. The primary energy used per unit of output is measured as EI, which takes into account the heat duty of reboilers and heaters (Pazmino-Mayorga et al., 2021). WC represents the water consumed per product output. CO₂ emissions for utility production, i.e. steam, are directly evaluated with the Aspen Plus tools. A value of 0.34 kgCO_{2eq}/kW_{el} is selected to assess the emission intensity of electricity for pumps and compressors. This data is averaged for the EU countries and it is reported from the European Environmental Agency (2023).

MI, E_F, EI, and WC metrics are defined as follows:

$$MI = \frac{\text{Raw materials mass} - \text{Final products mass}}{\text{Final products mass}} \tag{13}$$

$$E_{factor} = \frac{\text{Waste amount}}{\text{Final product mass}} \quad (14)$$

$$EI = \frac{\text{Overall process duties}}{\text{Final product mass}} \quad (15)$$

$$WC = \frac{\text{Water consumption (incl. CT losses)}}{\text{Final product mass}} \quad (16)$$

Additionally, sustainability metrics were normalized using kg of biogas feedstock as functional unit.

2.2. Economic analysis

Capital Expenditures (CAPEX), Operating Expenditures (OPEX), and income are considered for evaluating the economic performance. CAPEX is estimated using the Guthrie method (Bailie and Whiting, 1998). Bare module cost (C_{BM}) is actualized for the 2019, to avoid consideration of the economic perturbations caused by the recent geopolitical and pandemic situation.

$$C_{BM_{act}} = C_{BM} \frac{CEPCI_{2019}}{CEPCI_{2001}} \quad (17)$$

Chemical Engineering Plant Cost Index (CEPCI) in 2019 was reported to have a value of 607.5 (Chemical Engineering, 2019). OPEX includes direct costs (e.g. raw materials, utilities, and wastewater treatment) and fixed costs (e.g. depreciation and taxes) considered for Net Present Value (NPV). Utility consumption is computed using Aspen Plus. Parameters for the economic evaluation are retrieved from Turton handbook (Bailie and Whiting, 1998). Biogas costs as raw material are taken from IEA report (IEA, 2020). The annual operating time has been assumed equal to 8000 h. Yearly revenues mainly concern fuel-grade DME and methanol sales. Methanex (methanex, n.d.) is a reliable reference for methanol prices, while DME selling costs are taken from the Asian Market ("Dimethylether price Market," 2021). Payback time (PBT) is computed to evaluate the process. The PBT is defined as the time required to recover the initial capital investment in the plant:

$$PBT = \frac{CAPEX}{\text{Annual Revenues} - OPEX} \quad (18)$$

Cash flow analysis (CFA) is carried out to assess the process viability of both configurations. Eight cash flow analyses are performed to highlight the differences between process configurations A and B, considering:

- DME selling price with or without governmental incentives (subsidies).
- New construction or revamped plants.

Economic incentives are to be considered up to 10 years of plant lifetime, and after this period, DME sales are only subjected to its market value. Assumptions and equations related to CFA are reported in the *Supplementary Information*.

3. Results and discussion

This section deals with the technical, environmental, and economical results of the proposed process configurations. The results are described for all three process sections. The components conversion, hydrogen yields and DME selectivity are investigated and used to evaluate the technical performance of the direct DME production from biogas. CAPEX and OPEX breakdown and cash flow analysis are used to further examine the process economic feasibility, while sustainability metrics are used for the evaluation of the environmental impact of the process.

Table 2
Operating conditions of the main equipment.

Unit	Temperature [°C]	Pressure [MPa]	Molar composition	
Biogas compressor (Biogas)	IN 25.00	1.50	0.67 CH ₄	
	OUT 166.57		0.29 CO ₂	
Tri-Reformer (Bio-Syngas)	IN 500.00	1.28	0.04 O ₂	
			0.59 H ₂	
	OUT 950.00		0.24 CO	
			0.09 H ₂ O	
			0.07 CO ₂	
Syngas dryer (V-100)	25.00	1.25	0.01 CH ₄	
			0.65 H ₂	
			0.26 CO	
			0.08 CO ₂	
Syngas compressor	25.00	4.00	0.01 CH ₄	
	OUT 128.13		Same as above	
Syngas heater	IN 128.13	4.00	Same as above	
	OUT 235.00			
DME reactor	IN 235.00	3.80	A	B
	OUT 235.00		0.47 H ₂	0.47 H ₂
			0.35CO ₂	0.34 CO ₂
			0.06 CO	0.06 CO
			0.06 CH ₄	0.05 CH ₄
			0.02 DME	0.03
				DME
			0.01	0.01
			MeOH	MeOH

3.1. Technical performance

A total feed flowrate of 734 m³/h (5,872 mln m³/yr) of biogas at room condition is considered, with a composition of 67% CH₄, 29% CO₂, and 4% of O₂ (mol/mol). Several technical KPIs such as components conversions, yields, selectivity, and product purity were evaluated. Table 2 shows the main operating conditions of the reformer and the DME production section. These results are the same for both configurations as discussed earlier. Syngas heater and DME reactor work at the same temperature since the isothermal profile assumption is considered. The outlet molar composition of DME reactor is different, as reactant recycles depend on the purification strategies. In the reformer section, 96.2%, 27.3%, and 62% per pass conversions are achieved for CH₄, CO₂, and H₂O respectively. The hydrogen yield in the tri-reformer unit is 83.95%. This parameter is calculated as follows:

The obtained CO₂ conversion is lower than the values mentioned in the literature based on biogas reforming (Zhao et al., 2020). This is likely due to a lower activity of DR reaction compared to SR one. Indeed, an H₂/CO syngas ratio of 2.46 confirms this hypothesis. H₂/CO ratio are closer to unit when DR reaction is kinetically predominant. A lower amount of water in the reactants is required to favour such condition. DME reactor performances highlight some analogies between the configurations A and B. Table 3 depicts the design parameters for the synthesis reactor for both the configurations. Overall conversions of 96.4% and 89.1% are obtained for CO and H₂ respectively. Configuration A shows a higher CO₂ conversion (60.2%) than for Configuration B (55.2%). This difference leads to higher CO₂ emissions for the latter case. The evaluated DME selectivity towards methanol is 85.5% (case A) and 100% (case B). Note that the DME selectivity is rather meaningless for configuration B, as all the methanol produced is recycled back to

Table 3
RECS design parameters for the configuration A,B.

	Lenght	Tubes diameter	No. of tubes	Catalyst volume	Void fraction	GHSV	Coolant
A	8m	0.05 m	500	4.8 m ³	0.39	3816 h ⁻¹	BFW
B	8m	0.05 m	520	5.0 m ³	0.39	3802 h ⁻¹	BFW

Table 4
Main design parameters of the purification's series of equipment.

Parameter	Configuration A	Configuration B	Utilities
V-101 Cooled separation vessel			
T	20.00 °C	20.00 °C	
Pressure	3.80 MPa	3.81 MPa	
Duty	−1990.00 kW	−2100.00 kW	ChW
COL-100 Water absorption column			
Overhead T	55.20 °C	55.20 °C	
Bottom T	233.85 °C	233.85 °C	
Pressure	3.80 MPa	3.80 MPa	
Reboiler duty	1416.00 kW	1425.00 kW	HPS
Stages	18	18	
COL-101 CO₂ purification column			
Overhead T	25.00 °C	25.00 °C	
Bottom T	240.00 °C	240 °C	
Pressure	3.79 MPa	3.79 MPa	
Condenser duty	−831.00 kW	−782.00 kW	ChW
Reboiler duty	1084.00 kW	1056.00 kW	HPS
Stages	35	37	
COL-102 DME production column			
Overhead T	25 °C	25 °C	
Bottom T	155 °C	154 °C	
Pressure	0.60 MPa	0.60 MPa	
Condenser duty	−1504.00 kW	−1593.00 kW	ChW
Reboiler duty	821.00 kW	893.00 kW	MPS
Stages	35	31	
COL-101 Methanol separation column			
Overhead T	63.00 °C	65.00 °C	
Bottom T	100.00 °C	100.00 °C	
Pressure	0.10 MPa	0.10 MPa	
Condenser duty	−954 kW	−980 kW	CW
Reboiler duty	627 kW	649 kW	LPS
Stages	30	27	

enhance the DME yields. In the case A, the CO_x conversion (Equation (11)) is distributed to produce DME (85%) and methanol (15%) respectively. In the other case, the entire CO_x fraction is forced to the conversion in DME trough the recycle stream.

This recycle gives discrepancy on the results of downstream section for the two process designs.

Table 4 highlights the main design parameters of the equipment and the utilities involved in the purification section. High and medium pressure steam (HPS and MPS) are needed to reach the desired reboiler temperature. The condenser works with Chilled Water (ChW) to achieve an average temperature of 20 °C. The operating temperature of V-101 allows the condensation of 25% of the total DME in the liquid stream. This operation decreases the workload of the further columns and prevents the use of refrigeration and high water consumption. In the COL-100 process water contacts the outlet gases from V-101 condensing the unrecovered DME. Light gases are recycled back in the synthesis loop while 97% of DME is recovered. A flowrate of 230 kmol/h (4140 kg/h) of water is used to absorb the DME in both configurations. COL-101 removes the CO₂ content in the DME-methanol-water mixture. CO₂ recycling flowrates are around 886 and 975 kg/h for the two layouts.

Table 5
Sustainability metrics of the two process configurations.

Sustainability metric	Configuration A	Configuration B
Material Intensity (MI)	0.07 kg _{IN} /kg _(DME + MeOH)	0.07 kg _{IN} /kg _{DME}
	0.09 kg _{IN} /kg _{Biogas}	0.10 kg _{IN} /kg _{Biogas}
Energy Intensity (EI)	14.5 kWh/kg _(DME + MeOH)	15.7 kWh/kg _{DME}
	19.28 kWh/kg _{Biogas}	22.29 kWh/kg _{Biogas}
Water consumption (WC)	38.15 kg _{H₂O} /kg _(DME + MeOH)	42.17 kg _{H₂O} /kg _{DME}
	50.74 kg _{H₂O} /kg _{Biogas}	59.88 kg _{H₂O} /kg _{Biogas}
E-Factor	0.43 kg _{WASTE} /kg _(DME + MeOH)	0.48 kg _{WASTE} /kg _{DME}
	0.57 kg _{WASTE} /kg _{Biogas}	0.68 kg _{WASTE} /kg _{Biogas}
CO ₂ emission per products	1.35 kg _{CO₂} /kg _(DME + MeOH)	1.50 kg _{CO₂} /kg _{DME}
	1.79 kg _{CO₂} /kg _{Biogas}	2.13 kg _{CO₂} /kg _{Biogas}

Note: Configurations A and B require 1.33 and 1.42 kg_{Biogas}/kg_{product} respectively.

COL-102 rectifies the DME with the required purity and a recovery ratio of 99.97% (w/w) in both cases. The last column performs methanol separation from water. Methanol is recovered with AA grade specification (ASTM, 1998) in Configuration A, meeting commercial requirements. However, methanol purity in Configuration B is around 95% w/w. Because of the methanol recycling, which increases the molar flowrate to be purified, Configuration B has a higher overall heating and cooling duties. The productivity is 667 kg/h DME and 158 kg/h methanol for configuration A, and 776 kg/h DME for configuration B.

3.2. Sustainability metrics

This section reports the sustainability analysis results for the direct DME process. The study covers each of the three plant sections. After that, the results are aggregated for a general overview. The specific details for each section are provided in the *Supplementary Information*.

Table 5 gives an overview of the sustainability metrics for the two process configurations. Indexes for process configuration A are normalized with respect to the total production of DME and methanol. Configuration B has slightly higher energy intensity and water consumption. The difference in water consumption can be attributed to the RECS section and the design of column COL-101. Notably, 1.33 and 1.42 kg_{Biogas}/kg_{product} are the amounts of fed biogas required to produce 1 kg of final product for configurations A, B respectively. In the configuration A, the final product is a mixture of methanol and DME while it is only pure DME in the process configuration B.

Configuration A and B emit 1.35–1.5 kg_{CO₂}/kg_{product} respectively. These values give good perspectives compared to 2.96 kg_{CO₂}/kg_{DME} as emission rate from a coal-gasification plant for DME production (Kajaste et al., 2018). For the production capacity considered here, the newly proposed processes save around 9000 tpy of CO₂ emissions as compared to conventional ones.

Table 6 shows the CO₂ equivalent emission for each plant section. The CO₂ emissions are not equally distributed among the three steps. Biogas tri-reforming includes the environmental impact of biogas compression and reforming operations. As previously mentioned, the latter is negligible since the relative emissions are considered biogenic. The HEN avoids external heat integration and its associated emissions. The DME synthesis has an emitting rate of 148.94 and 176 kg_{CO₂}/h for configurations A and B, respectively. The main contributors are the syngas compressor and the heater E-102. Configuration B has a higher emission value since the steam consumption of the heater is larger than for configuration A. The DME reactor section is by far the most energy-intensive of the three sections, emitting 923.23–952.04 kg/h of CO₂. Indeed, steam generation for reboilers requires high natural gas consumption. Higher heating duty in process configuration B leads to an increase in CO₂ emissions compared to configuration A. Steam generation with biogas combustion is a viable solution to strongly reduce the environmental impact associated with downstream section. Based on the data retrieved from Turton handbook, 0.4 ton of natural gas are needed for HPS production (Bailie and Whiting, 1998), thus 800 m³/h of biogas allow having a fully sustainable plant for steam generation. The plant capacity is two times larger in this perspective scenario, but the emission product could be reduced to only 0.25 kg_{CO₂}/kg of product. Another option is the use of green electricity in steam boilers using electrodes, which are now well established and available on the market. For example, PARAT Halvorsen AS from Norway (www.parat.no) provides electrode boilers producing HP steam (up to 85 bar), with duties up to

Table 6
CO₂ emission rate for each plant configurations.

	Configuration A	Configuration B
Biogas Tri-reforming	41.59 kg _{CO₂} /h	41.59 kg _{CO₂} /h
DME Synthesis	148.94 kg _{CO₂} /h	171.76 kg _{CO₂} /h
Downstream section	923.23 kg _{CO₂} /h	952.04 kg _{CO₂} /h

75 MW in one compact design unit.

3.3. Economic analysis

The economic analysis evaluates the process viability, in addition to the promising technical and sustainability key indicators. The estimated accuracy of the results is $\pm 30\%$, and the project definition is within 1–15% since the estimation is defined as Class 4 according to the Association for the Advancement of Cost Estimating International (AACE International). Preliminary estimates are used to make coarse choices between design alternatives. They are based on limited cost data and design detail (Towler and Sinnott, 2012). Material and energy balances are retrieved from the Aspen Plus simulation results. CAPEX, OPEX, and revenues are estimated with the aforementioned methods. CAPEX estimation is 7.664 M€ and 8.204 M€ for Configuration A and B, respectively. Higher CAPEX in the second case is due to larger units and recycling. OPEX takes into account biogas utilization, supply of electrical and thermal energy, and water consumption costs. A larger thermal heating load and higher water consumption in configuration B lead to an increase in OPEX.

As the CAPEX and OPEX breakdown for Configurations A and B are identical, Fig. 8 shows the first one only. Reactors represent the most impacting cost, accounting for 47% of total CAPEX. RECS reactor is composed of three different pieces of equipment: two heat exchangers, and a plug flow reactor. The price of the three units is evaluated separately and summed in the CAPEX evaluation. OPEX breakdown identifies the steam consumption as the most expensive utility cost.

Payback time (PBT) and CFA are used as economic indicators of the process systems. A complete cash flow analysis is available in the *Supplementary Information*.

Table 7 shows the analysed cash flow scenarios reporting the financial indicators, i.e. PBT and NPV. Analysis results show that Cases A.1, A.2, B.1, B.2, are not economically feasible, but all the cases with an incentive (subsidy) show great profitability. Even though scenarios without incentive are not economically viable, some considerations must be taken. The main cause for the negative NPV is the small production capacity of the plant, restricted to that of a typical biogas farm.

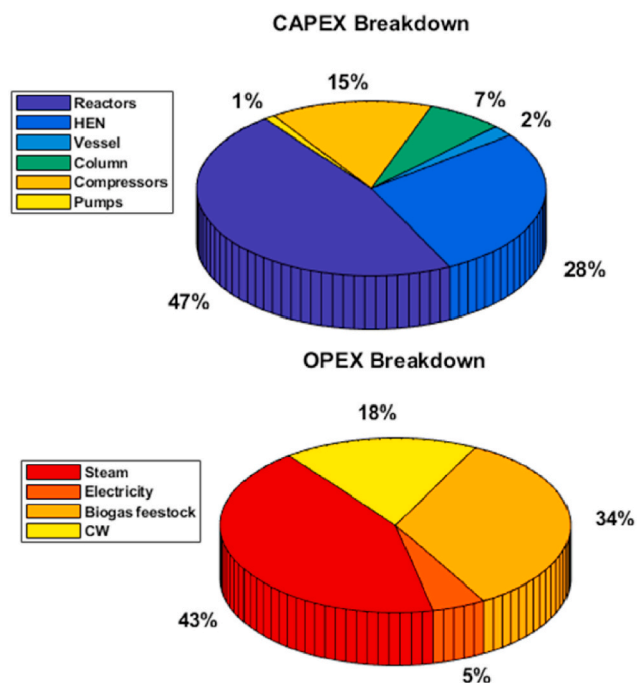


Fig. 8. CAPEX and OPEX breakdown.

Table 7

Cash flow scenario cases with PBT and NPV financial indicators.

Scenario	Configuration	Incentive	Plant construction	PBT [yr]	NPV (M€)
A.1	A	No	New	–	–1.85
A.2	A	No	Revamped	–	–0.44
A.3	A	Yes	New	6	9.23
A.4	A	Yes	Revamped	5	10.32
B.1	B	No	New	–	–2.97
B.2	B	No	Revamped	–	–0.98
B.3	B	Yes	New	5	10.19
B.4	B	Yes	Revamped	4	11.63

A capacity of minimum 10–20 kton/yr of DME would be more suitable than only 5–6 kton/yr, for a continuous production process and would benefit from the economy of scale. Furthermore, enhanced reactor design and catalytic bed composition could significantly increase the DME productivity. Another option to increase the DME production is to partially remove CO₂ with a CO₂ adsorption unit. Indeed, higher amount of CO₂ led to enhanced production of water according to Equation (8). Thus, it shifts the equilibrium of methanol dehydration towards reagents, limiting DME production. An additional problem of this compound is the larger design in the recycle section due to its limitations in conversion per single pass.

In the absence of an incentive, Configuration A is preferred as it gives the plant greater flexibility by producing both methanol and DME.

4. Conclusions and future perspectives

The direct DME production from biogas requires specific separation and purification operations, due to the large amounts of unreacted gases (CO, H₂, CO₂) in the reactor outlet mixture. New Cu–ZnO–ZrO₂ and Ferrite catalysts were employed to reach 49% of CO₂ overall conversion in the system. Yet, the downstream operations turn out to be the main process bottleneck. This problem has been addressed in this paper with a decision tree optimization to identify the best purification strategies, taking into account the costs and the utility type. Different separation units, and combinations of them were successfully tested and two process configurations (A, B) are the results of this methodology. The proposed processes use cooling water and steam as utilities, avoiding refrigerants and harmful adsorbents or solvents. The difference between the two process configurations is the final utilization of the produced methanol. Process Configuration A converts 8.8 kton/yr of biogas to 5.3 kton/yr of DME and 1.3 kton/yr of methanol, while Configuration B converts the same feed into 6.2 kton/yr of DME. The final product specification is 99.99 %wt for DME and 99.85 %wt for methanol. Biogas is considered a key contributor to future energy and to strengthen this concept, the two process configurations were evaluated in terms of sustainability and economic metrics, which clearly proved that a cleaner production of DME is possible.

Biogas composition is strongly related to the type of raw material utilized in the production. The methane content changes in a wide range, from 40 to 70 % v/v. In this work, biogas is produced from maize silage, corresponding to a methane content of 67% v/v (Smart et al., 2020). Available methane in biogas affects the outcome of the process. In case of lower quality of the biogas, less methane is available in the system leading to an overall decrease of DME production. Moreover, higher amount of CO₂ increases the size of the recycle section equipment with a consequence increasing of fixed costs. A sensitivity analysis based on biogas quality is a short-term perspective of this work. The outcomes of the analysis are interesting to decrease the uncertainty related to this process.

The sustainability analysis reveals a material intensity of 0.09–0.10 kg_{in}/kg_{Biogas}, an E-factor of 0.57–0.68 kg_{waste}/kg_{prod}, an overall energy intensity of 19.28–22.29 kWh/kg_{Biogas}, water consumption of 50.74–459.88 kg_{H2O}/kg_{Biogas}, and CO₂ emissions of 1.79–2.13 kg_{CO2}/

kg_{Biogas}. Even for this small production capacity, the newly proposed process saves 9000 tpy of emitted CO₂ as compared to the classic DME synthesis from coal gasification. The CO₂ emission associated with reformer fired heater are negligible since they come from a biogenic source. The most impacting utility for the CO₂ emission is the steam generation for the column reboilers, which account for 1000 kg_{CO2}/h produced. A fully sustainable plant could be designed to completely outdo this contribution, by producing steam from biogas.

Despite the promising technical performance and sustainability metrics, the results of the economic analysis do not support DME production without incentives (subsidies). NPV is negative for all cases without incentives, and the payback time is economically unfeasible. These outcomes suggest that Configuration A is the preferred one, in the absence of incentives and is a better option in terms of flexibility given by the production of two chemicals. Increasing the biogas farm capacity and the process production capacity is a viable solution to bridge the economical gap and benefit from the economy of scale. On the other hand, process profitability is achieved with the introduction of governmental policies. The best-case scenario is Configuration B with a PBT of 4 years and a NPV of around 12 million €.

The follow-up of this work aims to further optimize the overall plant in terms of economic and environmental aspects, and CO₂ utilization. A sensitivity analysis of the tri-reformer operating conditions is needed to find the optimal point to enhance CO₂ conversion, and the work of [Osat and Shojaati\(2022\)](#) showed that this parameter reaches ~99% with specific strategies. For the downstream process, the investigation of membrane separations or reactive distillation could be also beneficial for the direct DME production from biogas. Moreover, a limitation to overcome is the uncertainty in several aspects of the processes such as the supply chain and the environmental footprint. These points could be the object of medium-term perspective analysis focused on life cycle assessment of the biogas to bio-DME technologies including all the supply chain aspects. The results will be helpful to assess the overall feasibility of the process.

CRedit authorship contribution statement

M. Fedeli: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Data curation. **F. Negri:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation. **A. Bor-nazzini:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **L. Mon-tastruc:** Writing – review & editing, Validation, Supervision. **F. Man-enti:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Anton A. Kiss:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

List of abbreviations

AD	Anaerobic Digestion
BFW	Boiler FeedWater
CAPEX	Capital expenditures
CFA	CashFlow Analysis
CHP	Combined Heat & Power

ChW	Chilled Water
DME	Dymethyl-ether
DR	Dry Reforming
E _f	Environmental Factor
EI	Energy Intensity
GHSV	Gas Hourly Space Velocity
GWP	Global Warming Potential
HPC	Heat, Power, and Chemicals
HPS	High Pressure Steam
KPI	Key Performance Indicator
LCA	Lyfe Cycle Assessment
LPG	Liquefied petroleum gas
MDC	Methanol Dehydration Catalyst
MI	Material Intensity
MPS	Medium Pressure Steam
MSC	Methanol Synthesis Catalyst
NPV	Net Present Value
NRTL	Non-Random Two Liquid
PFR	Plug Flow Reactor
POX	Partial OXidation
RKS	Redlich-Kwong-Soave
SMR	Steam Methane Reforming
UNFCCC	United Nations Framework Convention on Climate Change
WC	Water Consumption
WGS	Water Gas Shift

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2024.141060>.

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