A versatile modular plant for converting biogas into advanced biofuels

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Research Article

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A versatile modular plant for converting biogas into advanced biofuels

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Abstract
The patented technology is a novel, portable, non-invasive, and flexible technical solution for converting biogas into valuable chemical compounds, such as bio-methanol and bio-dimethyl ether (bio-DME). It consists of compact modules, connected to each other through a flange-valve-flange system, to be installed downstream an existing traditional biogas plant.

The two main sections of the module are those of reforming and synthesis: in the first the biogas is converted into bio-syngas (H₂/CO/CO₂), while in the second the bio-syngas is transformed into advanced biofuels such as bio-methanol and bio-DME. Parts of the synthesis module can always be changed with small investments to switch the final products, according to local market needs and price volatilities.

Downstream at the synthesis section, it is possible to add a module for the separation and the purification of the chemical products.

The technology has been validated at the 0.15 MWe industrial scale.

Keywords
Biogas conversion; bio-methanol; bio-dimethyl ether; bio-syngas; carbon dioxide utilization; advanced biofuels
## Specifications Table

<table>
<thead>
<tr>
<th><strong>Subject code</strong></th>
<th>1500 General Chemical Engineering</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Specific subject area</strong></td>
<td>The invention can be classified as an industrial process for the treatment and conversion of biogas (methane and carbon dioxide mixture) into valuable products, such as methanol, dimethyl ether, acetic acid, and formaldehyde.</td>
</tr>
<tr>
<td><strong>Industry code</strong></td>
<td>C10G 2/00 (IPC/CPC): Production of liquid hydrocarbon mixtures of undefined composition from oxides of carbon.</td>
</tr>
<tr>
<td><strong>Details of inventors</strong></td>
<td>Flavio Manenti (<a href="mailto:flavio.manenti@polimi.it">flavio.manenti@polimi.it</a>) - Politecnico di Milano</td>
</tr>
<tr>
<td><strong>Dates of invention</strong></td>
<td>The invention was conceived in October 1\textsuperscript{st} 2016 and put into practise in 2017. A demonstration plant has been on-stream since August 2022, to validate the efficacy of this technology at the industrial scale.</td>
</tr>
<tr>
<td><strong>Patent details</strong></td>
<td>The Italian patent application was filed on June 30\textsuperscript{th}, 2017, and published with the number: 102017000073797</td>
</tr>
<tr>
<td></td>
<td>Date patent granted: September 30\textsuperscript{th}, 2019</td>
</tr>
<tr>
<td></td>
<td>Patent owner: Politecnico di Milano</td>
</tr>
<tr>
<td></td>
<td>Patent attorney or agent: Raffaella Asensio (Perani &amp; Partners)</td>
</tr>
<tr>
<td></td>
<td>Contact for service: Massimo Barbieri</td>
</tr>
<tr>
<td></td>
<td>Claiming the national patent application, an international patent application was filed on July 2\textsuperscript{nd}, 2018, with the number PCT/IB2018/054895 and published on January 3\textsuperscript{rd}, 2019, with the number: WO 2019/003213 A1) (now expired).</td>
</tr>
<tr>
<td></td>
<td>After the end of the PCT procedure, a United States (filing No. 16/627,003) and a European patent application (filing No. 18747017.4) were filed. Both applications were published with the number US2020222874A1 and EP3645666A1 respectively.</td>
</tr>
<tr>
<td></td>
<td>An Office Action was received, and the examination phase is still in progress for both applications.</td>
</tr>
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</table>
A further Italian patent application (divisional) was filed on September 19th, 2019, and published with the number 102019000016775

Date patent granted: September 20th, 2021
Patent owner: Politecnico di Milano
Patent attorney or agent: Raffaella Asensio (Perani & Partners)
Contact for service: Massimo Barbieri

### Intended use

The Italian patent has been optioned by a company operating in the renewable energy field.
The other family members (EP and US applications) are available for licensing.

### Funding / sponsor acknowledgments

This invention received a specific grant by a company for the construction of a demonstration plant. The project is continuing with the implementation of a 1MWe industrial plant. Agreement with 19 biogas plants for their refurbishing into bio-methanol production is ongoing in Po Valley (Italy).

### Related research article

None.

### Related other sources: (datasets, software, diagrams, plans, etc.)

None.

### Value of the invention

- Ease of installation: it does not require any changes to already existing biogas plants to be made.
- Easy reproducibility: installation of the same module in different biogas farms.
- Production of advanced biofuels such as bio-methanol, and bio-DME: higher selling price than electrical energy and biomethane options.
• High production flexibility: being a modular system, at any time and with a minimum investment it is possible to replace the final synthesis product. Bio-methanol to bio-DME production is performed in 24h.

• Carbon negative process: -88% for bio-methanol and -87% for bio-DME syntheses if the final products are used as base chemicals.

• Global process yield: 1kg MeOH/ 1 kg biogas processed (according to the biogas quality).

• Energy self-sufficiency, which occurs a few cycles after starting.

• Process circularity: the produced chemicals can replace the conventional fuel used for feedstock transportation. Possible partial decarbonization of primary and tertiary sectors.

Invention Description

The BIGSQUID (BiOGas-to-liQUID) technology consists of a module of approximately 5x3x3 m, which is positioned downstream of the traditional plant to produce biogas, without any plant invasiveness or the need for modifications to the existing plant. The dimensions are such that each section (or the entire module) can be containerized and shipped.

The biogas stream flows into the module in whole or in part, which is then transformed into bio-methanol, bio-dimethyl ether, but also in bio-acetic acid or other organic compounds. Thanks to its modularity, this production can be planned according to the needs of the local market.

Figure 1 shows the block flow diagram (BFD) for biogas to bio-methanol, or bio-DME, process. The modularity of BIGSQUID gives flexibility to produce different chemicals. In the BFD, the CO₂ stream is purified from the valuable chemicals and potentially sold as food-grade CO₂ following E290 European legislation. The configuration of the downstream section changes depending on the chemical production.

Figure 1 BIGSQUID block flow diagram
Methanol is a light, volatile, colourless, and flammable liquid that is polar at room temperature and is miscible in water and many organic solvents. The main uses include the production of formaldehyde, MTBE/TAME, acetic acid and DME. Methanol is mainly synthesized from natural gas and coal; the reaction is exothermic and favoured by high pressures and low temperatures [1].

The worldwide production of methanol was 100 Mt/y in 2020 with a forecast demand of more than 150 Mt/y in 2040 [2].

DME (H₃C-O-CH₃), the simplest ether, is not a greenhouse gas, it is colourless, highly flammable at ambient temperature and pressure conditions; it has properties like those of liquefied petroleum gas (LPG).

Having a high cetane number, dimethyl ether can be used in diesel engines as a substitute for diesel. Despite its lower viscosity, an important feature is that it does not form particulate matter during combustion. It is produced mainly by converting natural gas into synthesis gas (CO+H₂) and by converting such syngas in DME through two main pathways. One possibility is the two-step (or indirect) route, in which syngas is first converted into methanol in a dedicated reactor and then this molecule is dehydrated in a different unit, leading to DME production. Another possibility is the one-step (or direct) route, in which syngas is directly converted into a mixture of CO₂, H₂O, methanol and DME in the same reactor. The module uses the one-step technology for the synthesis of DME, the design of which was specifically optimized for maximizing the final product yield [3].

DME can also be converted into synthetic olefins and hydrocarbons.

Finally, acetic acid, perhaps the most important of the carboxylic acids, is produced industrially through the carbonylation process of methanol (the most used method), or by oxidation of acetaldehyde, ethanol, or short-chain hydrocarbons.

The two main sections of the module are those of reforming and synthesis: in the former one the biogas is converted into bio-syngas (H₂/CO/CO₂), while in the latter one the bio-syngas is in turn transformed into hydrocarbon compounds having few carbon atoms, such as bio-methanol, bio-DME, bio acetic acid and formaldehyde.

The reactions involved in reforming are essentially three:

A. Dry reforming  \( CH₄ + CO₂ \rightarrow 2H₂ + 2CO \)

B. Steam reforming  \( CH₄ + H₂O \rightarrow 3H₂ + CO \)

C. Water Gas Shift  \( CO + H₂O \rightarrow CO₂ + H₂ \)

The reforming section operates at a pressure between 5 and 15 bar, in a temperature range between 750 - 900 °C, in the presence of platinum and rhodium-based catalysts.

Since the reaction is endothermic, the necessary energy is provided either by the engine already installed in the biogas plant or by direct supply to the reforming firebox. There are two different options for heat supply: the combustion of a small part of the biogas from the anaerobic digester or the combustion of the process tail gas, which is rich in unconverted H₂, CO, and CH₄.

The reactions involved in the synthesis step for the production of bio-methanol are the following:

D.  \( 2H₂ + CO \rightarrow CH₃OH \)

E.  \( 3H₂ + CO₂ \rightarrow CH₃OH + H₂O \)
F. \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

To increase the reaction yield to 35% by volume, catalysts based on zinc and copper oxides supported on \( \gamma \)-alumina have been developed.

As regards the synthesis of bio-acetic acid, the reaction used is that of carbonylation of bio-methanol:

G. \[ \text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH} \]

The standard process includes two reactors, tubular catalytic for methanol and slurry for acetic acid. The catalysts used are based on Cu-ZnO-Al\(_2\)O\(_3\) or Cu-Zn-ZrO\(_2\) in the presence of Ga\(_2\)O\(_3\). The reaction is carried out at temperatures between 220 ° - 250 °C and at a pressure of 5 - 15 bar.

With regards to the conversion of biogas into bio-dimethyl ether, it is necessary to use catalysts that operate in situ for obtaining the dehydration of bio-methanol according to the reaction:

H. \[ 2 \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \]

With 563 kg/h of biogas fed to the module, 422 kg/h of bio-DME are obtained, with a total yield of 75%.

With regards to the downstream of the synthesis section, it is possible to add a module for purification, separation and possibly a section consisting of at least one of the following units: compression, lamination, heat exchange, water gas shift (WGS, useful for correcting the ratio \( \text{H}_2/\text{CO} \) of the syngas in the event that methanol is to be synthesized), absorption at oscillating pressure (PSA, useful for recovering the hydrogen produced), solid oxide fuel cells (SOFC), burners, membrane systems (for separation water) and medium pressure steam units (MPS).

**BIGSQUID simulation**

Previously to BIGSQUID technology installation in Fattoria Autonoma Tabacchi (Tobacco Farm, FAT), the biological process was analyzed with a feasibility study, process modelling, and variable optimization. Aspen HYSYS v11 was used as a tool for these kinds of operations. Figure 2 shows the Aspen HYSYS layout of BIGSQUID technology. The inlet biogas was chosen as equal to 1 MWe in a conventional biogas cogeneration plant. The thermodynamic model chosen for the simulation was Soave–Redlich–Kwong (SRK), which is very well suited for methanol properties. Biogas was purified from \( \text{H}_2\text{S} \) traces with adsorbent filters. This operation was useful to avoid several problems related to \( \text{H}_2\text{S} \) such as reactor catalysts poisoning, tube corrosion and the plant’s overall performance lowering. After upgrading, biogas was sent to a b-stadium compressor to reach a pressure of around 15 bar. Afterwards, the clean biogas was mixed with pressurized water (@15 bar) and sent to a feed-effluent heat exchanger. The ratio of steam/biogas was different and was dependent on the chemical production choice. This unit recovered the produced syngas hot enthalpy by heating the biogas-water mixture. The reforming reactor was modelled as HYSYS plug flow reactor with Xu-Froment heterogeneous kinetic model. The reactor working conditions are reported in Table 1. Fuels burned in the HYSYS fired heater model sustained the endothermicity of reforming reactions. Hot products exiting from the reformer unit, syngas mixture, were cooled down in three different steps: (i) feed-effluent exchanger, (ii) air cooler, and (iii) cooling water heat exchanger. This last unit lowers the syngas temperature leading to water condensation in a specific separator vessel. The recovered water was recycled back to the reformer unit optimizing water
consumption. After the de-watering unit, syngas was compressed, by a single-stadium compressor, to the working pressure of the methanol synthesis.

Before entering the synthesis section, bio-syngas was washed with cooling water to favor the absorption of CO$_2$ present in bio-syngas. This step was useful to adjust the syngas stoichiometric number, defined as:

$$SN = \frac{x_{H2} - x_{CO2}}{x_{CO2} + x_{CO}}$$

To increase and maximize the performance of bio-methanol and bio-DME production, the SN optimal value is around 2.05 [1]. Since the control of this parameter at the exit of the reforming section is unfeasible, a specified section is needed to adjust this value.

This system was divided into 2 columns:

- The first column worked at high pressure to increase the absorption of CO$_2$ in water, and the humid syngas exit at the top of the column poor in acid gas. A liquid stream, acid water, was sent to the second column.
- The second column worked at room conditions desorbing the CO$_2$ from the water. Lean water was recycled back closing the loop of this section.

After syngas conditioning, the gas was heated with a process-process heat exchanger exploiting the exiting hot product from the methanol reactor.

Bio-methanol/DME converter is a plug flow reactor-heat exchanger composed of two sections:

- Catalytic: Tubes are filled with Copper Zinc Aluminum Oxide (CZA) catalyst which favors the conversion of reactants into methanol. In the case of bio-DME production, the CZA catalytic bed is mixed with $\gamma$-Al$_2$O$_3$ powder to improve the MeOH dehydration to bio-DME according to reaction H.
- Thermal: Tube bundles are inside a shell with cooling fluid, this ensures heat removal management leading to a quasi-isothermal profile along the reactor. The heat removal is also present in bio-DME production since the bio-MeOH dehydration is exothermic too. The difference lies in heat management, this led to a different strategy in the cooling operations.

The unit was modelled as a HYSYS plug flow reactor with refitted Graaf’s heterogeneous kinetic model, proposed in the work of Bisotti et al (2022) [4].

The hot products, rich in methanol and unconverted syngas, were cooled with (i) process-process heat exchanger, (ii) air cooler, and (iii) cooling water heat exchanger. At this operating condition, the methanol-water mixture condensed in the separator vessel while unconverted syngas was recycled back in the methanol loop synthesis. In the case of bio-DME production, the separation step required more cooling enthalpy due to different thermodynamic properties.

Part of these light gases, rich in H$_2$ and CO, could be used as fuel for the reforming firebox leading to a circular process without any need for fossil fuel supply.

Below, Tables 1-2 show the material balances of the main process streams and the most important key performance indicators.

The simulation was customized for BIGSQUID bio-methanol synthesis, the parameters associated to bio-DME production require a further optimization analysis, which will be the target of future publications.
### Table 1 Material properties of the main process streams

<table>
<thead>
<tr>
<th>Streams</th>
<th>Molar Flow</th>
<th>T</th>
<th>P</th>
<th>xCH₄</th>
<th>xH₂</th>
<th>xCO</th>
<th>xCO₂</th>
<th>xH₂O</th>
<th>xCH₃OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>UOM</td>
<td>Nm³/h</td>
<td>°C</td>
<td>bar</td>
<td>%v</td>
<td>%v</td>
<td>%v</td>
<td>%v</td>
<td>%v</td>
<td>%v</td>
</tr>
<tr>
<td>Biogas</td>
<td>400</td>
<td>25</td>
<td>1.5</td>
<td>62.0</td>
<td>-</td>
<td>-</td>
<td>38.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bio-Syngas</td>
<td>1053</td>
<td>35</td>
<td>15</td>
<td>0.7</td>
<td>40.5</td>
<td>16.9</td>
<td>6.9</td>
<td>35.1</td>
<td>-</td>
</tr>
<tr>
<td>Clean Syngas</td>
<td>1000</td>
<td>20</td>
<td>60</td>
<td>1.1</td>
<td>65.4</td>
<td>27.2</td>
<td>6.2</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Unconverted gases</td>
<td>65</td>
<td>8</td>
<td>58</td>
<td>13.8</td>
<td>63.4</td>
<td>9.7</td>
<td>12.8</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>Bio-Methanol</td>
<td>351</td>
<td>8</td>
<td>58</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
<td>7.9</td>
<td>7.8</td>
<td>83.6</td>
</tr>
</tbody>
</table>

### Table 2 Main BIGSQUID key performance indicators

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reformer unit operating conditions</strong></td>
<td>950°C-15 bar</td>
</tr>
<tr>
<td><strong>Bio-MeOH synthesis operating conditions</strong></td>
<td>250°C-60 bar</td>
</tr>
<tr>
<td><strong>Bio-MeOH yearly production</strong></td>
<td>4.3 kt/y</td>
</tr>
<tr>
<td><strong>Biogas Yield</strong></td>
<td>86.07%</td>
</tr>
<tr>
<td><strong>Heat Circularity</strong></td>
<td>48.7%</td>
</tr>
<tr>
<td><strong>Electrical Power</strong></td>
<td>208 kW</td>
</tr>
<tr>
<td><strong>CO₂ utilization</strong></td>
<td>88%</td>
</tr>
<tr>
<td><strong>Bio-DME yearly production</strong></td>
<td>3.0 kt/y</td>
</tr>
</tbody>
</table>

*Switching final chemical production

Biogas yield is a parameter useful to understand the BIGSQUID performance. It is computed as methanol production related to the process of inlet biogas. The lower massive bio-DME production is justified by the bio-methanol dehydration step as in reaction H.
The various sections are connected to each other by hydraulic-mechanical devices (valve/flange/valve type) and therefore are easily modular. The synthesis process was validated through a pilot plant set up at the university laboratories, initially using commercial catalysts (CZA) and then modified with CaO, MgO and SrO as promoters [5]

The first industrial validation at 0.15 MWe was recently conducted Città di Castello (PG, Italy) in collaboration with FAT. Figure 3 shows a construction phase of the industrial plant on the courtesy of FAT.

The project will continue with the implementation of a 1 MWe industrial scale module.
Background

A preliminary state-of-the-art search was conducted in-house, using the Orbit Intelligence database, to make sure that the invention proposal met the patentability requirements. [6,7, 8]. The EPO examiner, who carried out the patentability search on behalf of UIBM, listed five prior art documents in the Search Report of the Italian patent application:

- D1: EP 2 659 960 [9]
- D4: WO 2016/101076 [12]
- D5: GB 2545474 [13]

None of the cited references contained all the features written in the first claim of the patent application. At the end of a careful analysis of the prior art documents, the following considerations were made to prove the novelty requirement of the invention:

- Documents D1, D4 and D5 used biogas as a feedstock.
- Only D4 considered the anhydrous reforming, while other patents mentioned syngas production through steam reforming and partial oxidation.
- D1, D2, D4 and D5 used the Fischer Tropsch process for the synthesis of hydrocarbons and value-added products. Only D4 claimed the production of methanol and dimethyl ether.
- D1, D2 and D4 disclosed the replacement of some plant sections, but for a different scope (e.g., the substitution of the exhaust catalyst or the removal of a blockage in pipes): the section was not replaced with a different one.
- Contrary to what was asserted in the Written Opinion, neither D3 nor D5 provided for the use of a modular system.

However, to overcome novelty, inventive step and clarity objections, process claims were converted into plant claims. Moreover, the value-added products obtainable according to the invention were specified in the first claim of the patent application.

The objective technical problem solved by the invention amended in such a way consisted in obtaining a more versatile industrial plant.

The main and distinctive technical feature of the invention is that a section can be replaced by another one, specific to produce a value-added chemical compound. Moreover, the claimed section had lower dimensions compared to those disclosed in D1-D5 patents. Each section is connected by means of a flange–valve–flange system.

The technical effect achieved is the possibility to adopt this technology in those farms hosting a biogas plant used for internal energy production.

From an environmental point of view, the invention can improve CO₂ sequestration: in fact, a biogas plant that produces 1MW of electric energy, releases 3141 t/y of CO₂ in the atmosphere directly from the purification section, while the remaining 4711 t/y of CO₂ are emitted due to household uses.

The same considerations were made by the examiner in the PCT phase: even if a PCT Direct Letter was filed, the examiner added a new document in the Search Report (D6: WO 2016/179476 [14]), not mentioned in the previous report.
A new set of claims were submitted in the European regional phase to overcome the objections brought up in the PCT Written Opinion.

The sole prior art document disclosing plants for the conversion of biogas with replaceable sections was D2 which, however, claimed the conversion of syngas into synthetic fuels. Moreover, D2 reported the replacement of identical modules only in order to obtain the same type of products and not different ones. None of the prior references (D1-D6) explicitly disclosed connection devices of the valve-flange-valve type.

The examination is still in progress.

In the first Office Action, the USPTO examiner underlined two further pieces of prior art references, not previously cited in the EPO report:

- Hwang (US 2009/0035192) [15]
- Reinke (US 2005/0178063) [16]

The application was classified with the following CPC classification symbols: B01J19/0014, 0013,245, H01M8/1231, 618, C01B3/48, 53 (main trunk symbols), B01J2219/0004 (indexing code), C01B2203/0233, 0238, 0283, 042, 061, 066, 0822, 107, 1241.

Considering the examiner’s objections, a new set of claims was written. Also, in this case the examination is still in progress.

### Application potential

The invention can be applied to those countries that have intensive farming. The biogas plant is advantageous above all for the farms where the plant is installed and the biogas is produced starting from a first-generation biomass by using anaerobic fermentation/digestion, as well as for multi-utilities, due to the incentives received from the electricity supply companies.

In Italy, biogas production is a well-established reality, with 1823 operating plants. A 1 MWe plant that supplies for example a biogas with 60% CH₄ and 40% CO₂ by volume, leads to a profit in electricity sold at a flat market price. As in Table 3, with 0.11 €/kWh produced, the income for 8400 h/y of operations is 0.924 M€/y. considering an incentive equal to 0.12 €/kWh (Italian incentive for biogas plants installed since 2013), the total income achieves 1.932 M€/y. As baseline reference case, it is worth considering a CAPEX of 4.5 M€ for the installation of the plant and an OPEX in the order of 1 M€/y including feedstock, harvesting, and maintenance. It is apparent that the whole sector cannot survive without the incentives and incentives have a deadline: after 15y they expire.

A current alternative option to continue the production at the end of the incentives is the upgrading of the biogas to biomethane, in a way that it could be introduced into the gas network currently in use; it would prolong the incentives by 10y. Moreover, this would solve the complex problem linked to the non-transportability of biogas (too expensive to be applied) thanks to the exploitation of the national gas network infrastructure. Unfortunately, biomethane purification is a less desirable solution than biogas. In fact, a 1 MWe plant that supplies a common biogas is equivalent, in mass, to about 30% CH₄ and 70% CO₂. This inevitably leads to an exploitation of only 1/3 of the total biogas in weight and, as reported in Table 3, to a production of 2.5 kt/y of biomethane with a (pre-conflict) price of 0.15 €/kg, which leads to an
income of 0.375 M€/y. Accounting for the incentives, in the order of 0.60€/kg that is significantly larger than the biogas case, the total income for the biomethane production is 1.875 M€/y, which appears in any case in line with the biogas total income. Including an additional CAPEX of 3.0 M€ for the installation and commissioning of the biomethane plant and considering 1 M€/y of OPEX, it is a reasonable alternative to prolong the biogas sector life-term.

The invention is providing a new option. In the case of production of bio-hydrogen, bio-methanol and bio-DME, Table 3 is providing the comparative economics. In the case of bio-hydrogen, the BIGSQUID technology can produce 0.625 kt/y. Hydrogen of fossil origin has a (pre-conflict) price of 1.4 €/kg. In a conservative approach, it is possible not to take into consideration the additional value of the molecule coming from bio-sources, which could be in the order of +30-/+50%. The income is 0.875 M€/y, but no incentives are defined. Assuming a CAPEX of +4.5 M€ including the final compression stages for hydrogen (gas) storage and the same OPEX as above, this solution is unappealing. If the BIGSQUID technology is adopted for producing bio-methanol, the situation is completely different. The total production is 4.3 kt/y, since a good amount of CO₂ is also converted into the final product. With a (pre-conflict) market price of 0.525 €/kg, the income results in 2.1 M€/y, which is higher than the total income with incentives of the biogas, bio-methane, and bio-hydrogen productions. Considering the incentives on the bio-methanol synthesis equal to 0.36 €/kg (according to the Italian Decree of March 2nd, 2018), the total income achieves 3.540 M€/y. With a CAPEX of 4.5 M€ and OPEX not different from the previous options, the production of bio-methanol from biogas through BIGSQUID technology results economically appealing also without any incentive and strongly appealing in case of incentive. The production of bio-DME is smaller than the one of bio-methanol and it is equal to 3.0 kt/y due to the de-hydration related to Reaction H. The fossil (pre-conflict) price is 0.615 €/kg and to income is 1.845 M€/y. With the incentives of Italian government equal to 0.485 €/kg, the total income is 3.3 M€/y. Considering a CAPEX of 4.6 M€, slightly higher with respect to the methanol synthesis for the complexity of the purification section, the bio-DME synthesis is also an appealing solution, although less than the bio-methanol case.

Table 3 BIGSQUID Economics.

* Market (pre-conflict) price for the fossil molecule. Biomolecules are expected to have higher prices.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Production</th>
<th>Specific value</th>
<th>Income (8400 h/y)</th>
<th>Incentive (Italy)</th>
<th>Total income</th>
<th>CAPEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas</td>
<td>1 MWh</td>
<td>0.11 €/kWh</td>
<td>0.924 M€/y</td>
<td>0.12 €/kWh</td>
<td>1.932 M€/y</td>
<td>4.5 M€</td>
</tr>
<tr>
<td>Biomethane</td>
<td>2.5 kt/y</td>
<td>0.15 €/kg</td>
<td>0.375 M€/y</td>
<td>0.60€/kg</td>
<td>1.875 M€/y</td>
<td>+3.0 M€</td>
</tr>
<tr>
<td>BIGSQUID™ Bio-H₂</td>
<td>0.625 kt/y</td>
<td>1.4 €/kg*</td>
<td>0.875 M€/y</td>
<td>-</td>
<td>0.625 M€/y</td>
<td>+4.5 M€</td>
</tr>
<tr>
<td>BIGSQUID™ Bio-MeOH</td>
<td>4.3 kt/y</td>
<td>0.525 €/kg*</td>
<td>2.1 M€/y</td>
<td>0.36 €/kg</td>
<td>3.540 M€/y</td>
<td>+4.5 M€</td>
</tr>
<tr>
<td>BIGSQUID™ Bio-DME</td>
<td>3.0 kt/y</td>
<td>0.615 €/kg*</td>
<td>1.845 M€/y</td>
<td>0.485 €/kg</td>
<td>3.300 M€/y</td>
<td>+4.6 M€</td>
</tr>
</tbody>
</table>
**Ethics Statement**

The authors declare that they have upheld all ethical standards of Invention Disclosure during the entirety of their work on the disclosed invention.

**CRediT author statement**

**Flavio Manenti**: Conceptualization, Investigation, Supervision, Data curation and Writing - Original draft preparation  
**Massimo Barbieri**: Writing – Original draft preparation, Reviewing and Editing.  
**Francesco Negri**: Data curation, Writing - Reviewing and Editing.  
**Matteo Fedeli**: Data curation, Writing - Original draft preparation.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

**References**


