UPGRADING OF BIOGAS TECHNOLOGY THROUGH THE APPLICATION OF GAS HYDRATES

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ABSTRACT

Gas hydrates have been thoroughly studied for a long time mainly as an unconventional energy source and a nuisance in pipeline gas transport. Only recently the extraordinary capability of water to form Gas Hydrates has been proposed as a novel technology in gas handling, mainly as a gas storage and transport alternative and lastly as a promising technology for gaseous mixture separation and purification.

Biogas is a widely applied technology for the production of renewable Energy, with the lowest environmental impact and the highest energy conversion efficiency among the biomass energy conversion technologies, particularly suitable for the energy conversion of wet biomasses and biowastes.

Biogas, a mixture of gases mainly composed of CH₄ and CO₂ and small amounts of H₂S, is normally converted into Renewable Electric Power fuelling in Combined Heat and Power systems.

Nowadays, Biogas technology is moving towards the production of Biomethane along with Electric Power, an upgrading that requires the development of processes aimed at effectively storing and refining the Biogas.

The aim of the present work is to evaluate the applicability of Biogas Hydrates (BGH) formation as a novel technology for Biomethane production with particular attention to the plant scale applicability.

Particular attention has been paid to the embedding of the Gas Hydrate technology within the standard Biogas production technology both in terms of energy yields, economic balances and plant integration.

Interesting results have been obtained regarding the effect of Biogas composition on the BGH formation and on the efficiency Biogas separation.

The added value connected to the capability of treating Raw Biogas, obtaining directly stored undesired gas, has been also evaluated.

Keywords: Biogas Hydrates, Biogas Upgrading, Biomethane, Gas Mixtures, Energy Balance

INTRODUCTION

Biogas is one of the most important Renewable Energy Source, for its capability for continuous energy production, and the possibility to convert into Renewable Energy, very low grade feedstock, such as wet biomasses and biowastes, along with energy crops.

In the EU-27 Biogas Renewable Energy production increased from 2006 to 2009 from 16.97 TWh to 25.17 TWh equivalent to a growth of 48.3%. In 2009 the EU Biogas production

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capacity was about 15 Billion Nm\(^3\) namely 8.3 Million Tons of Oil Equivalent (Mtoe), and the outlook for the 2020 is a production potential of 15 Mtoe. Germany, biogas top producer in EU, points out to cover 1/6 of its Natural Gas (NG) dependency with Biogas production.\[^{1,2}\]

A Biogas plant produces Biogas by Anaerobic Digestion (AD) of the organic matter, while Biogas is directly converted to Renewable Electric Power (REP) by means of Combined Heat and Power (CHP) systems. The efficiency of CHP system ranges from 35\% to 40\% of the total energy input as Biogas LHV. Biogas is mainly composed of CH\(_4\), ranging from 60\%v/v to 70\% v/v by volume and CO\(_2\) ranging from 40\% v/v to 30\% v/v along with small amounts of H\(_2\)S generally not greater than 1\% v/v.

In recent years more attention has been focused on the upgrading of Biogas to Biomethane, a clean renewable fuel with a remarkable potential in the energy market. Biomethane is the most important biofuel due to the lowest environmental impact, being possible through Biomethane exploitation to obtain 49.8 MWh per hectare per annum (MWh/ha/\(\text{y}\)), more than three times in comparison to Biodiesel with 14.3 MWh/ha/\(\text{y}\) and Bioethanol with 15.1 MWh/ha/\(\text{y}\).\[^{3}\]

Biomethane production and injection into the NG grid is a fact. Germany, with more than 60 Biomethane production plant, in 2010 injected into the national NG grid more than 360 million Nm\(^3\) of Biomethane.\[^{2}\]

Biomethane is obtained from Biogas by removal of CO\(_2\) and other impurities, in order to reach a methane quality comparable to NG standards. Various technologies are known and applied to clean up the Raw Biogas to Biomethane, the most used being: Pressure Swing Adsorption (PSA), Water Scrubbing (WS), Organic Solvent Scrubbing (OSS), Membrane Separation (MS) and Cryogenic Upgrading (CU). The BIOGASMAX is a research project, financed under the EC policies of the FP6, for a more efficient production, distribution and use of biogas in the transport sector.\[^{4}\]

Anyway, all these technologies suffer from a scale factor, and are barely cost effective for small size plants, namely less than 1 MW\(_{\text{el}}\). On the other hand, Biogas incentive policies are favoring the building of small size 0.5-0.2 MW\(_{\text{el}}\) plants. So, the current policy and technology status seems to exclude small plant for the Biomethane production reducing the EU Biomethane production potential. Clathrate Hydrates of Gases, or Gas Hydrates for short, are self-assembling nanostructures made of water and gaseous molecules. Under proper conditions of pressure and temperature, water spontaneously organizes itself around a gas molecule (guest) forming a dodecahedral solid structure (host). Thus a Gas Hydrate is a solid water phase capable of trapping gases. Discovered as a nuisance in pipeline gas transports, where Gas Hydrates form inside the pipe plugging the same, natural occurrence of Natural Gas Hydrate (NGH) is common in seafloor where biogenic natural gas finds thermodynamic conditions that favor the formation of hydrates due to hydrostatic pressure and cold stream. The estimation of amount of NGH in nature is remarkable high, and accounts for more than twice the other fossil reserves. Thus NGH is classified as non-conventional energy source. The solid phase of a Gas Hydrate shows a phase equilibrium with its gaseous phase. For this, given a certain temperature, different gas molecules show different hydrate forming pressures. In various cases, the difference is wide enough to allow the resolution of gaseous mixture by inducing the selective formation of Gas Hydrate. Separation and recovery of CO\(_2\) from fuel and flue gas such as mixture of CO\(_2\)/H\(_2\) and CO\(_2\)/N\(_2\) have been proposed\[^{5,6}\]. Moreover, energy analysis for a practical application to a CO\(_2\)/H\(_2\) mixture has also been carried out and the energy cost for CO\(_2\) capturing through the formation of CO\(_2\) hydrate has been assessed\[^{7}\].

A continuous process for the removal of CO\(_2\) from syngas, based on selective hydrate formation, is the SIMTECHE, and has been developed by the NETL-DOE\[^{8}\]. Anyway, fuel gas mixture, such as syngas, and flue gas mixture, such as power plant exhausts, are not ideal for the separation through Gas Hydrates, due to the high temperature of the gas mixture at the production site, often over the 300\(^\circ\)C. A more interesting and suitable application of gas hydrate separation method could be the CO\(_2\) removal from a Raw Biogas, that is produced at a temperature lower than 35\(^\circ\)C, in order to produce Biomethane, a biofuel for which the infrastructure of usage and transport already exists. CH\(_4\) and CO\(_2\) form hydrates at quite different thermodynamic conditions insomuch that the possibility of recovering methane from NGH
reservoir by replacing the same with the more stable CO₂ hydrates, is widely investigated. Thus, it would be possible to recover CH₄ by storing CO₂ within a virtual zero carbon emission[9]. Nevertheless, the separation of a simple CH₄/CO₂ mixture has been poorly investigated and different interpretation can be found in literature.

CO₂ forms hydrates at milder condition than CH₄, thus the formation of CO₂ hydrate over CH₄ hydrate is thermodynamically preferred.[10] Moreover, the high solubility of CO₂ in water may favor the CO₂ hydrate formation kinetically.[11] Biogas Hydrate (BGH) formation has also been investigated as an energy storage system[12]. As a matter of fact Biogas, as a Natural Gas, may form a mixed hydrate, where both CO₂ and CH₄ are present in the hydrate crystal lattice, at an intermediate thermodynamic condition between those for CO₂ and CH₄. Thus, it would be possible to dissociate selectively a BGH in order to release one component and retain the other. However, the binary CH₄/CO₂ hydrate shows an unexpected dissociation kinetic behavior, where CO₂, the thermodynamically more stable component, is released firstly than CH₄.[13,14]

The aim of the present work is to evaluate the feasibility of Biogas upgrading through Gas Hydrate formation by analyzing the energy cost of the process and comparing the same with the existing technologies. Two different process approaches are proposed and analyzed: CO₂ Hydrate process, where only CO₂ hydrate is assumed to be forming from the Biogas mixture, thus capturing CO₂ in the hydrate structure and enriching the gas phase in CH₄. The other one is the Biogas Hydrate process, where it is assumed that Biogas can forms a mixed hydrate that than is selectively dissociated eliminating CO₂ from the hydrate phase and obtaining a purified Biomethane Hydrate. Conceptual picture of the two process approaches are reported in Figure 1 and Figure 3.

In order to simulate a typical Biogas composition, a mixture of 60%v/v of CH₄ and 40%v/v of CO₂ is assumed. Besides, it is also modeled a typical Raw Biogas composition, in which the presence of H₂S is introduced, thus simulating a composition of 60%v/v of CH₄, 39%v/v of CO₂ and 1% v/v of H₂S.

Equilibrium pressure and temperature profile are obtained for CO₂, CH₄, Biogas and Raw Biogas by using CSMHYD software and are plotted against CO₂ liquid/vapor equilibrium profile, and the operating pressure within the process. Line plot of the obtained profiles are reported in Figure 2 and Figure 4.

The hydrate formation process is divided into 5 section:

- Compression work
- Gas cooling
- Water cooling
- Hydrate formation heat removal
- Pumping and Mixing

The compression work is calculated as isoentropic work, assuming two compression stages with a roughly equivalent compression ratio. Iterative calculation method is used. Values of Cp and Cv at desired temperature are calculated by applying Langen’s linear equation. The efficiency of the compressor is set at 0.8.

The gas cooling power demand is calculated starting from 20°C, a typical Biogas outlet temperature, and cooled down to the desired hydrate forming temperature by means of an Heat Exchanger (Ex1) with a thermal exchange efficiency being set at 0.75.
Specific heat capacity, and density for the three pure components CH₄, CO₂ and H₂S are respectively 0.035, 0.037, 0.034 kJ×mol⁻¹×K⁻¹ and 0.68, 1.87, 1.47 kg/m³ at 15°C [15]. Values for the Biogas and Raw Biogas mixtures are approximated to the weighted average of the single components properties.

In the same way the water cooling power demand is calculated starting from 15°C and cooled down to the desired hydrate forming temperature by means of an Heat Exchanger (Ex2) with a thermal exchange efficiency of 0.75. The amount of water required for the formation of hydrates is calculated by assuming that all the three gases form an SI structure, with a Gas/Water stoichiometric ratio of 1:5.75. Full cavity occupancy is assumed and a rate of water conversion of 0.8 is chosen.

The amount of cooling power required for hydrate formation, at the hydrate forming temperature, is defined by the hydrate dissociation enthalpy for CH₄, CO₂ and H₂S, respectively 54.4, 73.0 [16] and 28.4 kJ/mol [17]. Hydrate dissociation enthalpy for Biogas and Raw Biogas mixtures are approximated to the weighted average of the single components dissociation enthalpy.

A 100 kWₑ of Biogas mini plant is evaluated equipped with a CCHP with Electric Power efficiency of 35% and thermal power efficiency of 55%. Due to the CCHP feature, such thermal energy can be divided into thermal power and cooling power in a desirable way. The Coefficient Of Performance (COP) of the chiller embedded in the CCHP system is chosen as 1.0 (typical 0.8 – 1.2). A 100 kWₑ Biogas plant needs to produce roughly 48.5 kg/h of Biogas.

Due to the hypothetical approach of the present work a well defined process layout cannot be provided, thus an exact calculation of the process energy demand for pumping and mixing cannot be provided. So pumping and mixing energy demand is assessed as the 5% of the entire process energy cost and considered as electric power, thus added to the electric power demand for compression. The heat for hydrate dissociation, where required, is not introduced into the calculation. The required high entropy heat can be easily recovered from a low grade heat source such as the sludge resulting from the digester, as reported in the Figure 1 and Figure 3 with Ex4.

**DISCUSSION**

**CO₂ Hydrate**

In this case it is assumed that CO₂ hydrate can form selectively from a Biogas mixture, thus enriching the mixture in CH₄. Conceptual picture of the process is reported in Figure 1. Biogas stream is split into two streams: one destined to Electric Power production by the CCHP while another is compressed to produce Biomethane by hydrate formation. Gas cooling power, water cooling power and the cooling power required for the removal of hydrate formation heat, is provided by the CCHP, respectively in the exchanger Ex1 and Ex2 and in the hydrate reactor HyForm.

The CO₂ hydrate formed is then transferred to the dissociation reactor HyDiss, and subsequently dissociated, thus recovering cooling power and cold water. The separated CO₂ is released into the atmosphere. It is not strictly required to capture or store the separated CO₂ because it results from biomasses with a zero carbon footprint. Further heat, potentially required for CO₂ hydrate dissociation, can be recovered from the digested sludge stream by means of the Ex4. The excess of heat in the CCHP is sent to the digester for temperature keeping. Further cooling power can be recovered by the Biomethane and CO₂ outlet streams. With this process approach a Biogas plant may produce Renewable Electric Power along with Biomethane.

![Figure 1 Conceptual picture of the CO₂ Hydrate process implemented in a classical Biogas plant equipped with a CCHP system](image)

Analyzing the chart in Figure 2 it is possible to observe that the equilibrium profile of CH₄ and CO₂ hydrates are well distant one from the other.
At 4°C the respective equilibrium pressures are 3.85 MPa and 1.98 MPa. Given a Biogas with a composition of 60%v/v CH₄ and 40%v/v CO₂, a pressure of 6.00 MPa is chosen as working pressure for the CO₂ Hydrate process, in order to have a CO₂ partial pressure of 2.40 MPa, enough for the formation of CO₂ hydrate and a CH₄ partial pressure of 3.60 MPa, not enough for the formation of CH₄ hydrate. Thus, the chosen working condition for the CO₂ Hydrate process approach is 4°C and 6.00 MPa.

![Figure 2](image)

**Figure 2** Identification of the CO₂ Hydrate process working conditions. ♦ CH₄ hydrate equilibrium, ♦ CO₂ hydrate equilibrium ♦ CO₂ liquid/vapor equilibrium. Solid line, process working pressure. Dashed and dotted lines respectively CH₄ and CO₂ partial pressure at the chosen process working pressure. Arrow, working temperature.

The compression process is divided into two stages, a first from 0.1 to 0.8 MPa with a compression ratio of 1:8 and a second from 0.8 to 6.0 MPa with a compression ratio of 1:7.5. The interstage cooling can be provided by recovering the heat for plant facilities. From the dissociation of CO₂ hydrate it is possible to recover cooling power and cold water for a new cycle of hydrate formation. The cooling power saving is estimated to be about 75% of the entire cooling power demand.

Upon the calculations made, the final energy cost for compression, pumping and mixing is 0.180 kWhₑₐ/kg Biogas electric power for each kg of treated Biogas, while the CO₂ capture energy cost is about 0.452 kWh/kg CO₂. Having NG about 13 kWh/kg as LHV, the Specific Energy Consumption (SEC) for the process would be 6.4% of the Biomethane energy content. However, due to the fact that cooling power is provided by the CCHP in a proper process integration, the electric energy needed to compression, pumping and mixing is the unique net energy cost required for Biogas upgrading, thus 0.509 kWhₑₐ/kgCH₄ with a SEC of only 3.9%.

A cooling power demand of 0.113 kWh/kg Biogas corresponds to 5.48 kW for the treatment of the entire hourly production of a 100 kWₑ Biogas plant, along with other 8.05 kWₑ accounted for compression pumping and mixing. Energy costs are summarized in Table 1.

<table>
<thead>
<tr>
<th>CO₂ Hydrate</th>
<th>kWh/kgCH₄</th>
<th>kWh/kgCO₂</th>
<th>kWh/kgBiogas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression</td>
<td>0.509</td>
<td>0.278</td>
<td>0.180</td>
</tr>
<tr>
<td>Cooling</td>
<td>0.320</td>
<td>0.174</td>
<td>0.113</td>
</tr>
<tr>
<td>Total</td>
<td>0.828</td>
<td>0.452</td>
<td>0.292</td>
</tr>
</tbody>
</table>

**Table 1** Calculated energy costs for the CO₂ Hydrate process, reported as kWh for each kg of: Biometane (CH₄), CO₂, Biogas.

**Biogas Hydrate**

In this case it is assumed that Biogas mixture forms completely a mixed hydrate that then is selectively dissociated in order to release CO₂ and retain CH₄. The process description, depicted in Figure 3, is analogous to that of the CO₂ Hydrate process, apart the recycling of the water required to form hydrates, from HyForm to HyDiss, in fact in this case it is assumed that CH₄ remains trapped as hydrate and a Biomethane hydrate is recovered. As for the CO₂ Hydrate process, the removed CO₂ is vented out to the atmosphere.

Chart in Figure 4 reports the equilibrium profile of a Biogas mixture with a composition of 60%v/v CH₄ and 40%v/v CO₂ at 2.0°C. The equilibrium pressure for the Biogas hydrate is 2.19 MPa. Choosing a process working pressure of 3.0 MPa, in which such a Biogas mixture shows an equilibrium pressure of 5.02°C would mean to have a subcooling of 2.98°C as driving force for the Biogas hydrate formation. The working condition for the Biogas Hydrate process has been chosen at 3.0 MPa and 2°C.
As for the CO$_2$ Hydrate, we have a two stages compression process, a first stage being from 0.1 to 0.5 MPa with a compression ratio of 1:5 and a second from 0.5 to 3.0 MPa with a compression ratio of 1:6. The interstage cooling can be provided by recovering the heat for the internal services of the plant.

From the selective dissociation of the Biogas hydrate only a little portion of the cooling power can be recovered with an estimate of 25%. This is mainly due to the fact that the CH$_4$ remains trapped in the hydrate. Consequently, the energy demand for cooling results remarkably higher than that for the CO$_2$ Hydrate process.

By the calculation carried out, the final energy cost for compression, pumping and mixing is 0.174 kWh$_{el}$/kg$_{Biogas}$ electric power for each kg of treated Biogas, while the final energy cost for cooling is 0.725 kWh$_{el}$/kg$_{Biogas}$ cooling power for each kg of treated Biogas, for an overall cost of 0.899 kWh$_{el}$/kg$_{Biogas}$. In terms of Biomethane production, the energy cost is 2.539 kWh$_{el}$/kg$_{CH_4}$, while the CO$_2$ removal energy cost is about 1.421 kWh$_{el}$/kg$_{CO_2}$. In this case the SEC for the Biomethane production would be 19.5%. It is much more evident the benefit resulting from the CCHP system. In fact, reporting such energy demands to a 100 kW$_{el}$ size Biogas plant, the electric power required for compression, pumping and mixing is 8.44 kW$_{el}$, while the cooling power required is about 35.2 kW, easily supplied from the CCHP system. Thus, in such case, the final cost for Biogas upgrading to Biomethane would be only electric power, being 0.174 kWh$_{el}$/kg$_{Biogas}$, namely 0.492 kWh$_{el}$/kg$_{CH_4}$ achieving a SEC of only 3.8%.

Energy costs are summarized in Table 2.

Summarizing the results, the energy cost for the production of Biomethane through the application of hydrate technology, with a proper process integration and exploiting the features of the CCHP systems, could range from 0.174 to 0.180 kWh$_{el}$/kg$_{Biogas}$.

<table>
<thead>
<tr>
<th>Biogas Hydrate</th>
<th>kWh/kg$_{CH_4}$</th>
<th>kWh/kg$_{CO_2}$</th>
<th>kWh/kg$_{Biogas}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression</td>
<td>0.492</td>
<td>0.275</td>
<td>0.174</td>
</tr>
<tr>
<td>Cooling</td>
<td>2.047</td>
<td>1.145</td>
<td>0.725</td>
</tr>
<tr>
<td>Total</td>
<td>2.539</td>
<td>1.421</td>
<td>0.899</td>
</tr>
</tbody>
</table>

Table 2 Calculated energy costs for the Biogas Hydrate process, reported as kWh for each kg of: Biometane (CH$_4$), CO$_2$, Biogas.

Such a cost is quite competitive when compared to other existing technologies\[^{18,19}\] for Biomethane production, showing an energy cost ranging from 0.174 to 0.639 kWh/kg$_{Biogas}$, as reported in Table 3 and Figure 5. The competitiveness of the CO$_2$ Hydrate and Biogas Hydrate processes is mainly due to their integrability with the existing technologies for Biogas production, such as the CCHP systems. Once compared to the widely applied WS process, the two processes result not
only energy effective, but also cost effective and with a lower environmental impact.

<table>
<thead>
<tr>
<th>Energy Costs kWh/kgBiogas</th>
<th>PSA</th>
<th>WS</th>
<th>OSS</th>
<th>MS</th>
<th>CU</th>
<th>Hy</th>
<th>Hy Tx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>0.209</td>
<td>0.174</td>
<td>0.174</td>
<td>0.284</td>
<td>0.174</td>
<td>0.087</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.235</td>
<td>0.260</td>
<td>0.582</td>
<td>0.200</td>
<td>0.639</td>
<td>0.180</td>
<td>0.090</td>
</tr>
</tbody>
</table>

Table 3 Comparison among the energy costs of various Biogas upgrading technologies: Hy means the processes proposed in the present work, HyTx means the processes proposed in the present work with the application of a Turbo Expander.

In fact, while the solubility of CO₂ in water ranges from 2-6 g/kg, even under moderate pressure, one kg of water under CO₂ hydrate forming conditions may capture up to 400g of CO₂, with a huge saving in terms of water usage. When we compare the results with the Cryoprocess, where Biogas is cooled down to the selective liquefaction of its components, we have to compare the latent heat of liquefaction (∆Hliq) with the latent heat of hydrate formation (∆Hhyd), generally significantly higher: for CO₂ ∆Hliq is 25.1 kJ/mol ∆Hhyd is 73.0 kJ/mol and for CH₄ ∆Hliq is 8.2 kJ/mol ∆Hhyd is 54.0 kJ/mol. It is also noteworthy that CO₂ can liquefy at -78.5°C while CH₄ liquefies at -161.6°C, extremely low temperatures once compared to the temperatures at which hydrates form, ranging from 0°C to 10°C, depending on pressure. Such extremely low temperatures do not allow for the usage of the CCHP systems. Thus the cooling power for such a latent heat, even small, must be entirely provided. The benefit of the Cryoprocess resides in the fact that the produced Biomethane and CO₂ are directly stored in a dense form. However, also the hydrate-based processes may allow the recovery of the separated gas in a stored form. As assumed in the Biogas Hydrate process, the obtained gas hydrate may capture and store Biomethane in a solid form, up to 200 times its volume, corresponding to a compression ratio of 1:200, and a mass storage capacity of about 13-15% w/w. For CO₂ such storage capacity would be 40-42% w/w. A further benefit from the CO₂ Hydrate and Biogas Hydrate processes is the possibility to obtaining the separated gas already in compressed form, due to the process working pressure. This can allow for the saving of a remarkable portion of the compression energy further required for feeding into NG grid or for the production of compressed Biomethane for refueling station.

In a process approach where the separated CO₂ is vented out into the atmosphere, it would be possible to recover the potential energy of the compressed gas by installing a Turbo Expander that allows for the conversion of the pressure drop into electric power. In the present work such a scenario has not been evaluated due to the small size of the plant analyzed, because the investment cost for a Turbo Expander would result uneconomical. Anyway, for a plant of bigger size, the use of a Turbo Expander may allow the saving of more than 50% of the compression energy cost[7], thus halving the process costs outlined in this work.

Raw Biogas also contains H₂S, a very powerful hydrate former. At 2°C pure H₂S forms SI structure hydrates at only 0.13 MPa, thus H₂S may affect remarkably the hydrate equilibrium, both for CO₂ Hydrate and Biogas Hydrate processes even at lower concentration such those typical of Raw Biogas. A Raw Biogas composition of 60%v/v CH₄, 39%v/v CO₂ and 1% v/v H₂S has been simulated and investigated such in the case of Biogas composition, see Figure 4. The result shows that the enthalpy of hydrate formation is affected in a negligible way, while the equilibrium pressure may be affected noticeably. For Biogas Hydrate process it would be possible to work at 2.5 MPa instead of 3.0 MPa. This results in a lower compression energy cost (5-6%). Anyway, the capability of the H₂S to form hydrates is very important. In fact, H₂S is the most undesired pollutant affecting Biomethane and the possibility of capturing it in a unique process along with CO₂ is very interesting. In the
The aim of the present work was to demonstrate how a gas hydrate based technology, for biogas upgrading, may result very promising in terms of: current technology compatibility, cost effectiveness, energy sustainability, and small scale applicability. The main benefit of the presented process approach resides in the fact that Biomethane can be produced along with the Renewable Electric Power, saving a remarkably quantity of energy by a proper process integration. In a next future scenario when Biomethane will receive incentives as biofuel, the production of Biomethane could result more profitable than CHP and allow the possibility of a production diversification, resulting in a smart market strategy. Given the energy cost for Biomethane production obtained with the present work, a plant energy balance has been carried out in order to find the proper amount of Biomethane and Electric Power that have to be produced in order to optimize plant integration and minimize energy costs.

For the CO₂ Hydrate process, by assuming to use of only 5% of the entire CCHP efficiency as cooling power, the minimum amount of Biogas that has to be burned in order to have enough cooling power capable to upgrading the remaining Biogas amount is only 28%. Thus, as reported in the chart in Figure 6, the plant could choose to produce Biomethane, along with Renewable Electric Energy from 0% to a maximum of 72%. Reporting this 28% to a 100 kWₑₐ plant means 28 kWₑₐ of Renewable Electric Power production along with an hourly Biomethane production of 12.3 Kg/h, enough to refuel a Biomethane fueled SUV each hour. The Electric Power consumption required for this Biomethane production is only 6.3 kWₑₐ of the 28 kWₑₐ produced.

![CO₂ Hydrate Process Balance](image)
The Electric Power consumption required for this Biomethane production is only 5.2 kWel of 38 kWel produced.

Is important to note that, as it is customer in Biomethane production plants, the thermal energy demand for the biodigester temperature keeping is not satisfied, anyway in the presented process approach a portion of heating power, resulting from CCHP, still remains available. Further thermal energy could be recovered by the catalytic combustion of the removed CO2 stream, also called “lean gas”, that normally still contain small amount of CH4.

**Figure 7** Biogas Hydrate process balance. ♦Electric and ♦Cooling power produced by converting a portion of Biogas in the CCHP system, versus the ♦Electric ad ♦Cooling power demand for the upgrading of the remaining Biogas portion. X axes reports the portion of Biogas addressed to Electric Power production

Thus, proper insulation design of the digester is required in Biomethane production plant. Also the integration with renewable systems for high-entropy heat, such as solar power systems can be desirable.

**CONCLUSION**

The feasibility for the application of a gas hydrates based technology for Biomethane production has been evaluated by means energy balance analysis. A proper process integration exploiting the cooling power of the CCHP system for the hydrate formation would result a promising strategy for plant engineering.

The results show that Biogas can be upgraded to Biomethane with two different process approach at an energy cost of only 174-180 kWhel/kg Biogas, namely with a SEC of 3.9 – 3.8%, thus resulting in a cost effective process. Biomethane can be produced along with Renewable Electric Power minimizing energy costs, and allowing the plant to embed a product diversification within the renewable energy market.

The proposed process approach would be also competitive in terms of reduced water consumption, lower maintenance cost, and small scale applicability.

Further investigation is required to establish the effectiveness of Biogas mixture resolving by application of selective gas hydrate formation or selective biogas hydrate dissociation. Proper plant design is required in order to minimize thermal energy demand for the thermal requirements of the digesters.

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