

UPGRADING BIOGAS QUALITY THROUGH THE APPLICATION OF GAS HYDRATES

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Abstract

For a long time gas hydrates have been investigated as a problem in pipeline gas transport and as potential energy source. This property 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 as the case of biogas, a mixture of gases mainly composed of CH₄ and CO₂ and small amounts of H₂S, is normally converted into Renewable Electric Power fuelling proper CHP (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 Crude Biogas, obtaining directly stored undesired gas, has 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 level feedstock, such as wet biomasses and bio wastes, along with energy crops.

In the EU-27 Biogas Renewable Energy production increased since 2006 to 2009 from 16.97 TWh to 25.17 TWh equivalent to a growth of 48.3%. In 2009 the EU Biogas production capacity was about 15 Billion Nm³ namely 8.3 Million Tons of Oil Equivalent (Mtoe), and the outlook for the 2020 is a production potential of 15Mtoe. Germany, the mayor producer of Biogas in EU, point out to cover 1/6 of its NG dependency with Biogas production.^{1,2}

A Biogas plant produces Biogas by Anaerobic Digestion of the organic matter, the Biogas is directly converted to Renewable Electric Power (REP) by means of Combined Heat and Power (CHP) systems. The efficiency of CHP system ranging from 35% to 40% of the total energy input as Biogas LHV.

Biogas is mainly composed by CH₄, ranging from 60%v/v to 70% v/v by volume and CO₂ ranging from 40% v/v to 30% v/v along with small amounts of H₂S generally not greater than 1% v/v. In the recent years more attention has been focused to 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 lowest lands impacts, in fact through Biomethane is possible to obtain 49.8 MWh per hectare per annum (MWh/ha/y), more than three times once compared

Biodiesel with 14.3 MWh/ha/y and Bioethanol with 15.1 MWh/ha/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 over 360 Million of Nm³ of Biomethane.²

Biomethane is obtained from Biogas by CO₂ and other impurity removal, in order to reach methane quality comparable to NG standards. Various technologies are known and applied to clean up the Crude Biogas to Biomethane, the most used are: Pressure Swing Adsorption (PSA) or 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 for a scale factor, and are barely cost effective for small size plant, namely less than 1MW_{el}. On the other hand, Biogas incentive pay policies are favoring the building of small size 0.5-0.2 MW_{el}. 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 more friendly called Gas Hydrates, are self-assembling nanostructure made by water and gaseous molecules. Under proper condition of pressure and temperature, water spontaneously organize itself around a gas molecule (guest) forming a dodecahedral solid structure (host), thus a Gas Hydrate is a solid water phase capable to trap gases.

Discovered as a nuisance in pipeline gas transport, where Gas Hydrate form inside the pipe plugging the same, natural occurrence of Natural Gas Hydrate (NGH) are common in seafloor where biogenic natural gas finds the thermodynamic hydrate forming condition due to hydrostatic pressure and cold stream. The estimation of amount of NGH in nature is remarkable high, and accounted for more than double of other fossil reserves, thus NGH are classified as non-conventional energy source.

The solid phase of a Gas Hydrate shows a phase equilibrium with its gaseous phase, thus given a certain temperature, different gases molecules shows different Hydrate Forming pressure.

In various cases the difference is wide enough to allow for resolving gaseous mixture by inducing selective formation of Gas Hydrate.

Separation and recovery of CO₂ from fuel and flue gas such as mixture of CO₂/H₂ and CO₂/N₂ have been proposed^{5,6}, moreover energy analysis for a practical application to a CO₂/H₂ mixture has been also carried out and energy cost for CO₂ capturing by CO₂ Hydrate formation has been assessed⁷.

A continue process, for CO₂ removal from syngas, called SIMTECHE, has been develop by the NETL-DOE⁸,

Anyway fuel gas mixture, such as syngas, and flue gas mixture, such as power plant exhaust, are not ideal for Gas Hydrates separation method, due to the high gas mixture temperature at the production site, often over the 300°C.

A more interesting and suitable application of gas hydrate separation method could be the CO₂ removal from a Crude Biogas, that is produced at a temperature lower than 35°C, in order to produce Biomethane, a biofuel for which the infrastructure of usage and transport already exist.

CH₄ and CO₂ forms hydrates at quite different thermodynamic condition insomuch as is widely investigated the possibility to recover methane from NGH reservoir replacing the same with CO₂ hydrates, more stable at the same condition. Thus would be possible to recover CH₄ storing CO₂ in a virtual zero carbon emission⁹.

Anyway the separation of a simple CH₄/CO₂ mixture is poorly investigated and in literature various interpretation are present.

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 investigates as energy storage system¹², in fact Biogas, as Natural Gas, may form a mixed hydrate, where both CO₂ and CH₄ are present into 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 analyzing the energy cost of the process and comparing the same with the existing technologies. Two different process approach are proposes and analyzed: CO₂ Hydrate process, where CO₂ Hydrate is formed selectively from the Biogas mixture, and the Biogas Hydrate where BGH are first formed and than selectively dissociated in order to release CO₂.

Analysis are based on 100KW_{el} Biogas mini-plant, in order to demonstrate the scalability of the process also for small size Biogas plants.

Process integration of a Gas Hydrate based Biogas upgrading technology is also evaluated focusing on the exploiting Tri-generation systems, namely a combined cooling, heat and power system (CCHP) where also cooling power is produced along with electric power and heat. A CCHP system allow for producing Electric Power at the same efficiency rate than a classical CHP system, but the embedding of an absorption chiller allow a CCHP for producing, along with heat, cooling power at a temperature ranging from 0° to 7°C, a temperature range easily exploitable for Hydrate formation.

METHOD

Energy analysis is proposed in the present work and compared with existing technologies. Based on literature analysis two different process approach are proposed and analyzed, the CO₂ Hydrate process, where only CO₂ Hydrate is assumed to form from the Biogas mixture, thus capturing CO₂ in the Hydrate structure and enriching the gas phase in CH₄. In the Biogas Hydrate process, instead, is assumed that Biogas can form a mixed Hydrate that than is selectively dissociated eliminating CO₂ from hydrate phase, obtaining a purified Biomethane Hydrate. Conceptual picture of the two process approach are reported in Figure 1 and Figure 3.

For simulating a typical Biogas composition, a mixture of 60%v/v of CH₄ and 40%v/v of CO₂ is assumed, moreover are also modeled a typical Crude Biogas composition, where 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 temperature profile are obtained for CO₂, CH₄, Biogas and Crude Biogas using CSMHY software, and plotted along with CO₂ liquid/vapor equilibrium profile, and processes operating pressure. Charts of the obtained profiles are reported in Figure 2 and Figure 4.

The hydrate formation process is divided in 5 section:

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

The compression work is calculated as isentropic work, assuming two compression stage of roughly equivalent compression ratio. Iterative calculation method is used, values of Cp and Cv at desired temperature are calculated by application of Langen's linear equation. The efficiency of the compressor is chosen at 0.8

The gas cooling power demand is calculated starting from 20°C a typical Biogas outlet temperature, and cooled down to desired hydrate forming temperature

by means of an Heat Exchanger (Ex1) with a thermal exchange efficiency chosen 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°C¹⁵. Values for the Biogas and Crude Biogas mixtures are approximated to the weighted average of the single component properties.

In the same way the water cooling power demand is calculated starting from 15°C and cooled down to 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 hydrate formation is calculated assuming that all the three gases form an SI structure, with a 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 hydrate forming temperature, is defined by the hydrate dissociation enthalpy for CH₄, CO₂ and H₂S, respectively 54.4, 73¹⁶ and 28.4 kJ×mol⁻¹¹⁷. Hydrate dissociation enthalpy for Biogas and Crude Biogas mixtures are approximated to the weighted average of the single component dissociation enthalpy.

A 100kW_{el} 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 CCHP system is chosen as 1.0 (typical 0.8 – 1.2). A 100kW_{el} Biogas plant need 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 low temperature heat can be easily recover from a low grade heat source such as the sludge resulting from the digester, as reported in the Figure 1 and Figure 2 with Ex4.

DISCUSSION

CO₂ Hydrate

In this case 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 streams is split in two streams, one destined to Electric Power production by the CCHP and another is compressed to Biomethane production by hydrate formation. Gas cooling power, water cooling power and the cooling power required for hydrate formation heat removal is provided by the CCHP, respectively in the exchanger Ex1 and Ex2 and into the hydrate reactor HyForm.

The CO₂ hydrated formed is transferred to the dissociation reactor HyDiss and than dissociated recovering cooling power and cold water. The

separated CO₂ is released to the atmosphere. Is not strictly required to capture or store the separated CO₂ because it results from biomasses with a zero carbon footprint. Further heat required for CO₂ hydrate dissociation can be recovered from the digested sludge stream by mean of the Ex4. The excess of Heat in the CCHP is addressed to the digester 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.

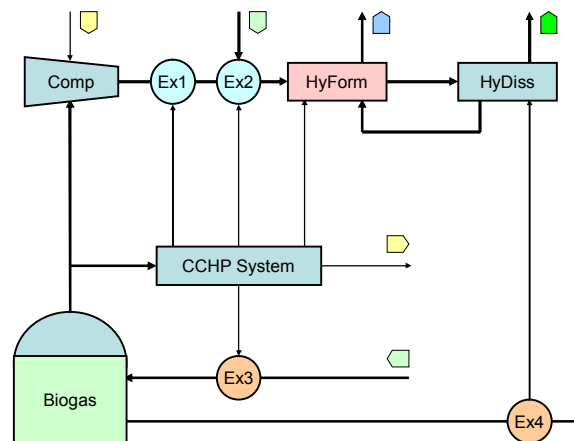


Figure 1

Analyzing the chart in Figure 2 is possible to observe that the equilibrium profile of CH₄ and CO₂ hydrates are well far each other, at 4°C the respective equilibrium pressures are 3.85 MPa and 1.98 MPa. Given the Biogas with a composition of 60%v/v of CH₄ and 40%v/v of 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 2.40MPa, enough for CO₂ hydrate formation, and a CH₄ partial pressure of 3.60MPa, not enough for CH₄ hydrate formation. A partial pressure of 2.40 MPa at 4°C for CO₂ hydrate correspond to a subcooling of about 1.63°C, as driving force for CO₂ hydrate formation. Thus the chosen working condition for the CO₂ Hydrate process approach are: 4°C and 6.00MPa.

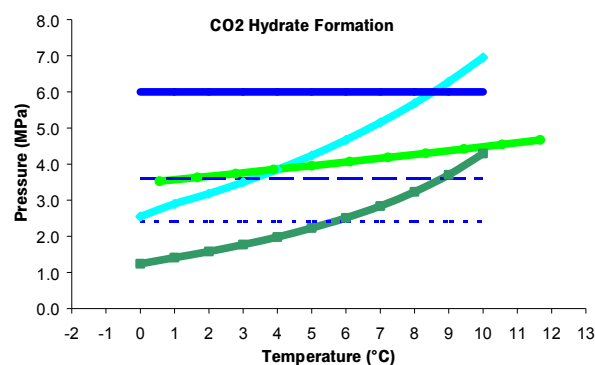


Figure 2

The compression process is divided in 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 recovering the heat for plant internal services.

From the CO_2 hydrate dissociation is possible recover cooling power and cold water for a new hydrate formation. The cooling power saving is assessed to be about the 75% of entire cooling power demand.

By the calculation carried out the final energy cost for compression, pumping and mixing is 0.180 kWh_{el}/kg_{Biogas} of electric power for each kg of treated Biogas, while the final energy cost for cooling is 0.113 kWh/kg_{Biogas} of cooling power for each kg of treated Biogas, for an overall cost of 0.292 kWh/kg_{Biogas} . In terms of Biomethane production the energy cost is 0.828 kWh/kg_{CH_4} , while the CO_2 capture energy cost is about 0.452 kWh/kg_{CO_2} .

Having NG about 13 kWh/kg as LHV, the Specific Energy Consumption (SEC) for the process would be the 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 the Biogas upgrading, thus 0.509 kWh_{el}/kg_{CH_4} with a SEC of only 3.9%. The 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 kW_{el} Biogas plant, along with other 8.05 kW_{el} for compression pumping and mixing. Energy costs are summarized in Table 1.

CO₂ Hydrate

| | KWh/Kg _{CH₄} | KWh/Kg _{CO₂} | KWh/Kg _{Biogas} |
|--------------|----------------------------------|----------------------------------|--------------------------|
| Compression | 0.509 | 0.278 | 0.180 |
| Cooling | 0.320 | 0.174 | 0.113 |
| Total | 0.828 | 0.452 | 0.292 |

Table 1

Biogas Hydrate

In this case is instead assumed that Biogas mixture form completely a mixed hydrate, and then selectively dissociated in order to release the CO_2 and retain the CH_4 . The process description, depicted in Figure 3, is analogous of the CO_2 Hydrate process, a part from the recycling of the water required to form hydrates, from HyForm to HyDiss, in fact in this case is assumed that CH_4 remain trapped into hydrate form and a BGH is recovered. As for the CO_2 Hydrate process, the removed CO_2 is vented to the atmosphere.

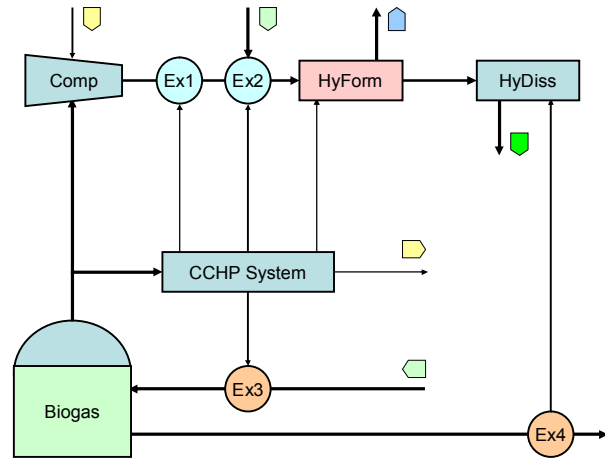


Figure 3

Chart in Figure 4 reports the equilibrium profile of a Biogas mixture with a composition of 60%v/v of CH_4 and 40%v/v of CO_2 , at 2.0°C. The equilibrium pressure for the Biogas Hydrate is 2.19 MPa. Choosing a process working pressure of 3.0MPa, where such Biogas mixture shows an equilibrium pressure of 5.02°C, would means to have a sub cooling of 2.98°C as driving force for the Biogas formation process. The working condition for the *Biogas Hydrate* process has been chosen at 3.0MPa and 2°C.

As for the CO_2 Hydrate, the compression process is of two stages, a first 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 recovering the heat for plant internal services.

From the selective dissociation of the Biogas hydrate only a little portion of the cooling power can be recovered assessed as the 25%, this is mainly due to the fact that the CH_4 remain trapped into the hydrate, thus the energy demand for cooling result remarkably higher than the same for the CO_2 Hydrate process.

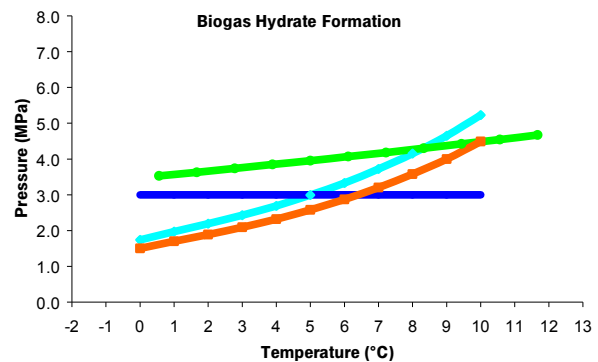


Figure 4

By the calculation carried out, the final energy cost for compression, pumping and mixing is 0.174 kWh_{el}/kg_{Biogas} of electric power for each kg of treated Biogas, while the final energy cost for cooling is 0.725 kWh/kg_{Biogas} of cooling power for each kg of treated Biogas, for an overall cost of 0.899 kWh/kg_{Biogas} . In terms of Biomethane production, the energy cost is 2.539 kWh/kg_{CH_4} , while the CO_2

removal energy cost is about 1.421 kWh/kg_{CO2}. In this case the SEC for the Biomethane production would be 19.5%. Is much more evident the benefit resulting from the CCHP system, in fact, reporting such energy demands to a 100kW_{el} size Biogas plant the electric power required for compression, pumping and mixing is 8.44kW_{el}, while the cooling power required is about 35.2 kW, easily supplied from the CCHP system.

Thus in such plant integration case, the final cost for Biogas upgrading to Biomethane would be the only electric power cost, namely 0.174 kWh_{el}/kg_{Biogas}. Energy costs are summarized in Table 2.

Summarizing the results, the energy cost for the production of Biomethane by application of hydrate technology, with a proper process integration and exploiting the features of the CCHP systems, could ranges from 0.174 to 0.180 kWh_{el}/kg_{Biogas}.

Biogas Hydrate

| | KWh/Kg _{CH4} | KWh/Kg _{CO2} | KWh/Kg _{Biogas} |
|--------------|-----------------------|-----------------------|--------------------------|
| Copression | 0.492 | 0.275 | 0.174 |
| Cooling | 2.047 | 1.145 | 0.725 |
| Total | 2.539 | 1.421 | 0.899 |

Table 2

Such cost is quite competitive with other existing technologies for Biomethane production, that shows an energy cost ranging from 0.174 to 0.639 kWh/kg_{Biogas}, as reported in Table3. The competitiveness of the *CO₂ Hydrate* and *Biogas Hydrate* processes is manly due to their integrability with the existing technologies for Biogas production such as the CCHP systems. Once compared with the widely applied WS process, the two processes result not only energy saving, but also cost effective and with a lower environmental impact.

| Costs | KWh/Kg _{Biogas} | | | | | | |
|-----------|--------------------------|----------|-----------|-----------|-----------|------------|--|
| PSA | WS | OSS | MS | CU | Hy | Hy TurboEx | |
| 209 - 235 | 174 - 260 | 582.0000 | 174 - 200 | 284 - 639 | 174 - 180 | 87-90 | |

Table 3

In fact while the solubility of CO₂ in water ranging from 2-6 g/kg, even under moderate pressure, a kg of water under CO₂ hydrate forming conditions may capture up to 400g of CO₂, with a huge saving in terms of water usage. Once compared with Cryoprocess, where the Biogas is cooled down up to the selective liquefaction of its components, is important to compare the latent heat of liquefaction (ΔH_{liq}) with the latent heat of hydrate formation (ΔH_{hyd}), generally quite grater: for CO₂ ΔH_{liq} is 25.1 kJ/mol ΔH_{hyd} is 73.0 kJ/mol and for CH₄ ΔH_{liq} is 8.2 kJ/mol ΔH_{hyd} is 54.0 kJ/mol. However is also important to note that the CO₂ can liquefy at -78.5°C while CH₄ at -161.6°C, temperatures extremely low once compared with the hydrate forming temperature ranging from 0°C to 10°C depending on the pressure. Such extremely low temperatures does not allow for the usage of the CCHP systems, thus such latent heat, even lower, must be entirely provided. The

benefit of the Cryoprocess resides in the fact the produced Biomethane and CO₂ are directly stored in a dense form, however also the hydrate based process may allow for recover the separated gas in a stored form. As assumed in the *Biogas Hydrate* process, the obtained gas hydrate may captures and stores CH₄, in a solid form, up to 200 times its volume, namely corresponding to a compression ratio of 1:200, corresponding to a mass storage capacity is about 13-15% w/w for CH₄ and 40-42% for CO₂. A further benefit of the CO₂ Hydrate and Biogas Hydrate processes is the possibility to obtain the separated gas already compressed, due to the process working pressure. This can allow for the saving of a lot of further compression energy required for NG grid feeding or Compressed Biomethane production for refueling station.

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

Crude Biogas also contain H₂S, a very powerful hydrate former, at 2°C, pure H₂S forms SI structure hydrates at only 0.13MPa, thus H₂S may affect remarkably the hydrate equilibrium, both for CO₂ Hydrate and Biogas Hydrate processes even at lower concentration such those typical for Crude Biogas. A Crude Biogas composition of 60%v/v of CH₄, 39%v/v of CO₂ and 1% v/v of H₂S, has been simulated and investigated as for the Biogas composition Figure 4. The result shows that the enthalpy of hydrate formation is effected in a negligible way, while the equilibrium pressure may be affected noticeably, for *Biogas Hydrate* process would be possible to work at 2.5 MPa instead than 3.0 MPa. This results in a lower compression energy cost, assessed at a reduction of 5-6%. Anyway the capability of the H₂S to form hydrates is very important, in fact H₂S is the most undesired pollutant of the Biomethane and the possibility to capture the same in a unique process along with CO₂ is very interesting. In the *CO₂ Hydrate* process the H₂S could trapped forming hydrates along with CO₂ and also helping the process, lowering the formation pressure. Also in the *Biogas Hydrate* process the presence of H₂S helps the formation of the mixed hydrate, anyway in this specific case the H₂S would probably remain trapper in the hydrate phase along with methane, and this would be ad undesirable side effect of the process. Thus concerning the *CO₂ Hydrate* process it would be suitable also for treating directly Crude Biogas, conversely for the *Biogas Hydrate* Process it would be better to treat a Biogas mixture where H₂S has been already removed. Other benefit on the implementation of an gas hydrates based biogas upgrading process is in that the process can use plain water and thus no gas drying is required, before the treatment.

Further pollutants, normally presents in the Biogas or Crude Biogas, may affect their hydrate forming behavior, such as Siloxanes, Mercaptans, Organic Halides, Ammonia and Particulate. Further investigations are required in order to define the effect of such pollutant on the capability of Biogas and Crude Biogas to form hydrates. Recent studies demonstrates how the use of thermodynamic stabilizer, such as THF or alkyl ammonium salts like TBAB and TBAF, may lower remarkably the hydrate forming pressure at a given temperature. Thus it would be possible to lower the working pressure both for *CO₂ Hydrate* and *Biogas Hydrate* processes, resulting in a further lowering of processes energy costs.¹⁸

The aim of the present work it 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 Renewable Electric Power at the same plant and in the same time, saving a remarkably energy cost by a proper processes integration. In a next future scenario where the Biomethane will receives incentive as biofuel, Biomethane production could results profitable over electric power, thus the possibility of a production diversification, as suggested in the present work would result 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 have to be produced in order to optimize plant integration and minimize energy costs. For the *CO₂ Hydrate* process, assuming to use only the 5% of the entire CCHP efficiency as cooling power, the minimum amount to Biogas that has to be burned in order to have a enough cooling power capable to upgrade the remaining Biogas amount, is the only 28%. Thus has reported in the chart of Figure5 the plant could chose to produce Biomethane, along to Renewable Electric Energy, from 0% to a maximum of 72%. Reporting this 28% to a 100kW_{el} plant, it means 28 kW_{el} of Renewable Electric Power production along with a hourly production of Biomethane of 12.3 Kg/h, enough to refuel a Biomethane fueled SUV each hour. The Electric Power consumption required for this Biomethane production are only 6.3 kW_{el} of the 28 kW_{el} produced.

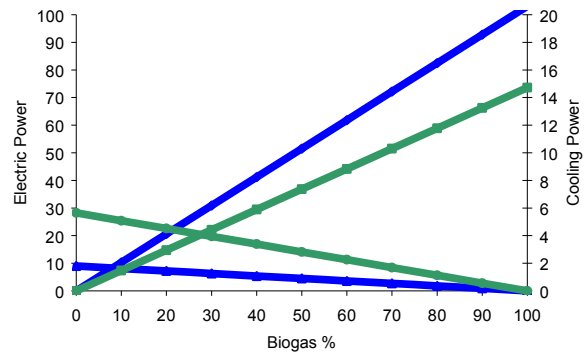


Figure 5

For the Biogas Hydrate process the cooling power demand is greater than that required for the *CO₂ Hydrate* process, thus a scenario where the electric efficiency of the CCHP is kept to 35% and the cooling efficiency the 20% is assumed. Also in this case Biomethane is produced along the Renewable Electric Power, a plant balance is reported in the chart of Figure6. Diverting the 38% of Biogas production to Renewable Electric Power the amount of cooling power recoverable by the CCHP system is enough to upgrade the remaining 62% of Biogas. Reporting this 38% to a 100kW_{el} plant, it means 38 kW_{el} of Renewable Electric Power production along with a hourly production of Biomethane of 10.6 Kg/h. The Electric Power consumption required for this Biomethane production are only 5.2 kW_{el} of the 38 kW_{el} produced.

Is important to note that, as is normal in Biomethane production plants, the energy demand for the biodigester temperature keeping is not satisfied, anyway in the presented process. approach a portion of heating power resulting from the CCHP still remain 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*.

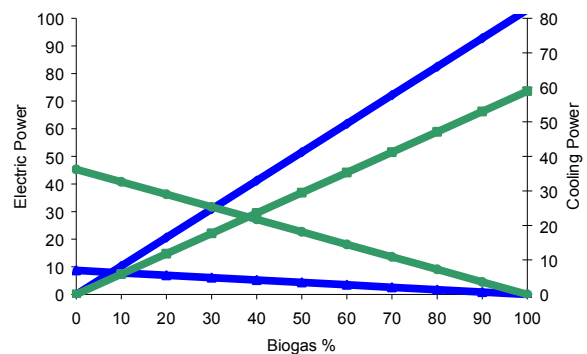


Figure 6

Thus proper digester insulation design is required in Biomethane production plant, also integration with renewable systems for low grade 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 energy balance analysis.

A proper process integration exploiting the cooling power of the CCHP system for the hydrate formation would result a promising plant strategy.

The results shows that Biogas can be upgraded to Biomethane with two different process approach at an energy cost of only 174-180kWh_{el}/kg_{Biogas} of Biogas, thus resulting in a cost effective process.

Biomethane can be produced along with Renewable Electric Power minimizing the energy costs for the both, and allowing the plant for a diversification of its products in 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 plat design is required in order to minimize thermal energy demand for digester temperature keeping.

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