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The Potential of Biogas; The Solution to Energy Storage

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Abstract: Energy storage will be a demand for balancing the renewable energy systems of tomorrow - especially when excess electricity from wind and solar power requires immediate utilization. Using biogas as a carbon source can generate CO_2-neutral carbon-based energy carriers, such as methane or methanol. Utilization of biogas today is limited to the generation of heat and power or biomethane (first generation upgrading), both processes disregarding the potential of the large amount of co-produced CO_2 during the fermentation process. Using renewable energy, biogas upgrading systems can convert the carbon dioxide to hydrocarbon-based high-density energy fuels which can replace fossil-based fuels for applications where they are hard to decarbonize. Here, the authors argue for future utilization possibilities of biogas and introduce the terminology of second generation upgrading to help research and development within this field. We believe that second generation upgrading of biogas will have a huge potential for dynamic energy storage.

Biogas

The market share of renewable energy resources is increasing [1]. Especially wind and solar power has increased tenfold globally from 2004 to 2014 [2]. Consequently, energy storage has become a growing challenge [3]. Several technologies have been proposed to assist in the need for energy storage, e.g. pumped storage hydroelectricity, compressed air energy storage, swing wheel storage, large scale batteries, etc. [4]. Nevertheless, efficient energy storage still remains a huge issue.

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Biogas has the potential to become the preferred solution to energy storage of the future. Biogas is produced from anaerobic breakdown of different biological feedstocks and generally consists of around 60% methane (CH_4) and 40% carbon dioxide (CO_2), with approximately 2000 ppm hydrogen sulphide (H_2S) as the main impurity. Independent of the downstream application of biogas, it is necessary to remove H_2S due to the corrosion and health issues involved. The majority of biogas plants produce combined heat and power (CHP), while a very small number (around 2% of all plants) produce biomethane [5]. For biomethane production, the CO_2 has to be removed from the biogas in order to ensure a high enough energy density in order to allow for injection in the natural gas grid. This is called biogas upgrading and CO_2 is a waste product from this process.
Future biogas upgrading technologies will need to consider CO_2 in biogas as an additional carbon source which could be used to increase the energy density in connection with efficient energy storage. In this way, electrical energy could be stored as either methane or liquid organic molecules through catalytic upgrading using renewable hydrogen (H_2) from electrolysis converting CO_2 into liquid fuel through e.g. Fischer-Tropsch-like processes.
Within the EU alone, the biogas energy production was 654 PJ in 2015 [6] and it continues to grow [5]. The biogas energy potential within Europa is estimated to be as high as 2.3×10^3 PJ by 2030 [6]. This corresponds to 15% of the total energy used for transportation in the EU in 2015 [7], and if the biogas is further upgraded using renewable H_2, this share could be even higher.
We believe that the use of biogas can be a key enabler when it comes to closing the carbon cycle. This would allow industries like e.g. aviation and long distance transport [8–10], which are not easily decarbonized, to convert into a sustainably future operating on green carbon-neutral fuel resources. However, these future applications of biogas lack a general term, and we therefore propose to use the term ‘second generation upgrading’ to describe those technologies, which use the CO_2 in biogas as the carbon source.

Upgrading Today; First Generation Upgrading

Today, biogas upgrading refers to the process of extracting CH_4 (biomethane) from biogas [11,12]. This process is necessary in order to make biogas suitable as a fuel for vehicles or injection into the natural gas grid [13]. Biomethane is known for its low carbon footprint, which can even be negative [14], making it highly attractive for several industries, such as the agricultural sector, the chemical industry, etc. Today, an industrial upgrading of biogas is solely first generation. The four main first generation upgrading technologies are [15]:

- Chemical scrubbing
- Water scrubbing
- Membrane separation
- Pressure swing adsorption

There are other emerging technologies, however, the above four are the market drivers.

First generation upgrading seeks to remove CO_2 as a waste product, although efforts are being made to create high-valuable food products from CO_2, using chemical scrubbing. The CO_2 could also be used for energy storage by combining it with hydrogen from electrolysis driven by renewable electricity from wind or solar power. Unfortunately, chemical scrubbing is quite energy intensive and there is no need to use a pure CO_2 stream in order to convert it to synthetic hydrocarbon when upgrading biogas. Removing the need for chemical scrubbing would significantly improve the overall energy efficiency of existing biogas upgrading systems [16].

First vs. Second Generation Upgrading

We believe the time has come to introduce the term 'second generation' upgrading as an alternative to 'first generation' upgrading that exists today.

Second generation upgrading refers to those technologies that utilize the biogas as a carbon source for storing energy. First generation upgrading uses methods, which only focus on the removal of CO_2 from biogas, while second generation upgrading technologies actively use the CO_2 to produce more carbon-containing energy carriers.

While the two generations of biogas upgrading have several differences of technical and scientific nature, the most efficient distinction between first and second generation biogas upgrading is:

- First generation do not utilize the CO_2 of the biogas
- Second generation uses the CO_2 as a carbon source

Significant research is being carried out into second generation biogas upgrading [17] (according to our terminology), although the current terminology does not allow distinguishing between first and second generation technologies. Moreover, completely different technologies are required for the second generation upgrading. The main differences are listed in the following sections.

CO_2 Utilization

Second generation upgrading makes use of CO_2 as an additional carbon source for energy storage. It is closely linked to the Carbon Capture and Utilization (CCU) technology, which is currently highly promoted, as necessary to reach zero-CO_2 policies [18]. It has become obvious that renewable energy supply cannot alone fulfil the wish for a CO_2 neutral society, and therefore, renewable energy should be supplemented by CO_2 storage or reuse of the CO_2 activities. CCU allows for a lowering of the carbon footprint to a certain extent with the need to use additional energy running the overall process.
Conversely, second generation biogas upgrading does not require energy-expensive carbon capture. The CO_2 in biogas is directly converted to hydrogen-carbon-containing molecules enabling a better overall energy efficiency [16].
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Maturity of the Second Generation Upgrading Technology

In our view, the current terminology on biogas upgrading constrains the economic support by favoring the simpler first generation technology. A new terminology would allow for a more clear focus on the energy storage possibilities of biogas and could help accelerate additional and necessary research and development in second generation upgrading technologies.

First generation upgrading is in use today, whereas second generation upgrading technologies remain in the demonstration phase. There is a clear need for innovative and cost-efficient technology development in second generation upgrading as it requires more expensive and complicated equipment as compared to first generation upgrading. The most promising technologies for second generation upgrading are discussed below.

Biogas as Carbon Source; Second Generation Upgrading

The conversion of CO_2 to biofuel or further conversion to synthetic fuel through Fischer-Tropsch catalytic synthesis is a research area that receives a great deal of attention [18]. Here, we present catalytic methanisation, methanol synthesis and biological conversion. Methanisation and methanol production are visualized in Figure 1, which shows how today's technology emits CO_2, while the application of tomorrow's 2nd generation technology uses energy in the form of H_2 to produce biofuels.
Common for all the second generation upgrading technologies discussed here is the need for renewable H_2. Renewable H_2 is produced by water electrolysis, mainly alkaline [19], and this technology has managed to be developed into a pluck-and-play technology characterized by both high efficiency and quick response time, which are of utmost importance when it comes to storage of renewable energy. While, flexible storage of excess energy as H_2 is a possibility, storage of the energy as either CH_4 or liquid organic molecules (HC; hydrocarbons) allows for further utilization of the stored energy within the liquid infrastructures already constructed. CH_4 can be stored and distributed in the natural gas grid and liquid organic molecules can be implemented in the transportation infrastructure. These applications also deviate from those of renewable H_2, since the energy density of the carbon-based storage is much higher as compared to that of H_2 [20].

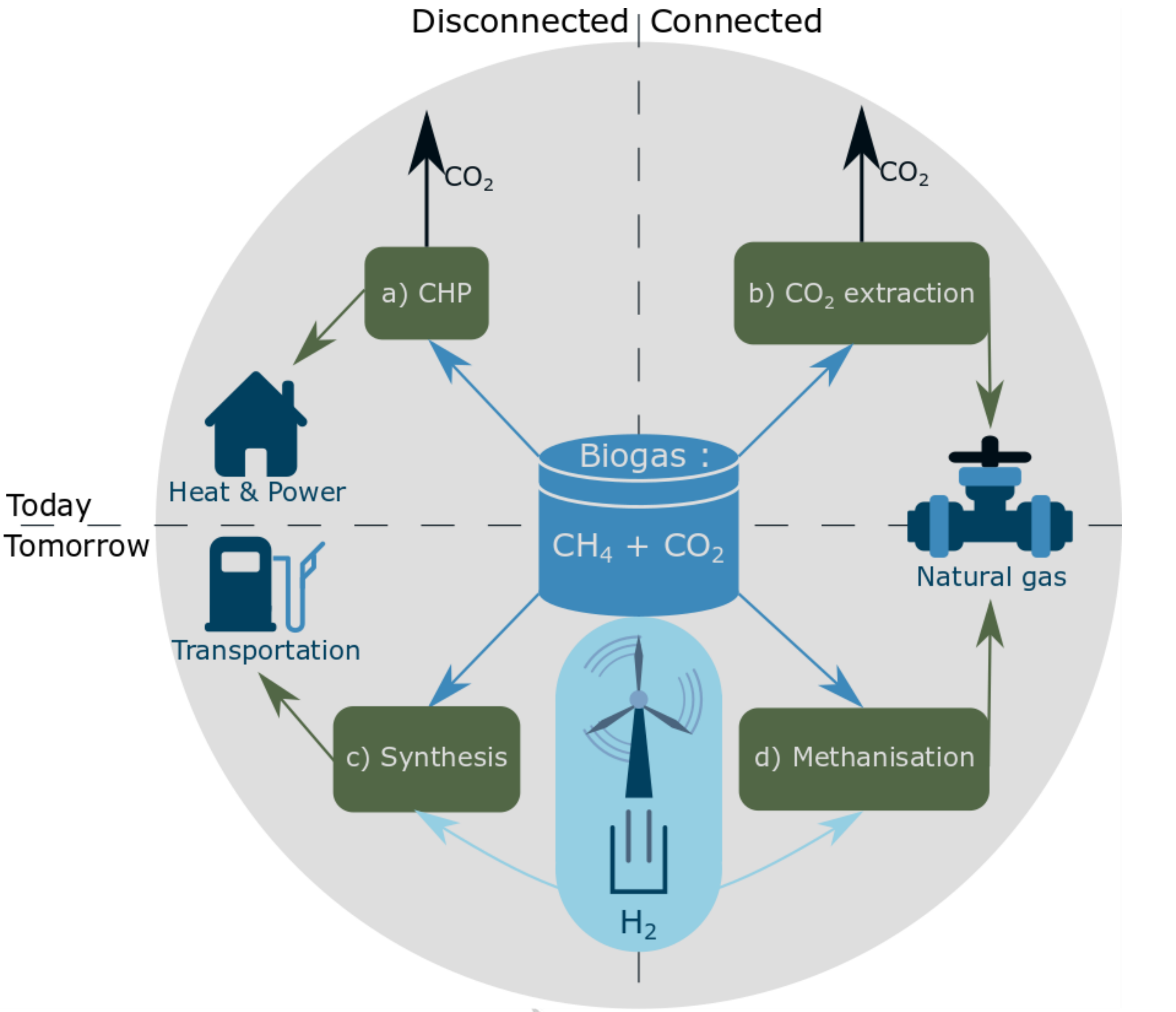

Figure 1: Biogas utilization. a) Combined heat and power system, most widely used application today. b) First generation upgrading, the methane is extracted from the biogas and supplied to the natural gas grid. Both c) and d) are second generation (2D) upgrading technologies, where the biogas is considered a carbon source as the CO_2 is converted using renewable hydrogen. c) Synthesis of liquid organic molecules, e.g. methanol, can be used in the transportation sector. d) Methanisation of CO_2, allowing energy storage in the natural gas grid

Catalytic Methanisation

Methanisation of biogas produces CH_4 from the CO_2 within the raw biogas. The catalytic methanisation process converts the CO_2 content to CH_4, using the Sabatier reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta G_{300\,°C} = -61.1 \text{ kJ/mol (eq. 1)}$$

This process was first discovered by Sabatier in 1913 and is most notably used today on the international space station to produce water [21]. Traditionally, the reaction is catalyzed over a high-surface-area nickel catalysts having both high selectivity and activity [22]. Desulfurized biogas could be used as a direct feedstock for the Sabatier reaction, since the CH_4 will act as an inert diluent which can be beneficial for the exothermic reaction due to its heat-distributing and -absorbent properties avoiding catalyst runaways [23].

The final product of first generation upgrading (biomethane) needs to have a low H_2S content. Dependent on the gas grid regulations, the requirement is usually below 4 ppm [24]. For catalytic upgrading, however, the restrictions are far more demanding, since H_2S is an irreversible poison for the catalysts used for CO_2 reduction [25,26]. Bartholomew et al. [27] found that concentrations as low as 1 to 10 ppb H_2S may result in considerable reduction of the catalyst activity, since the active surface sites react readily with H_2S, by a deactivation reaction [22]:

$$H_2S + NiO \rightarrow NiS + H_2O \qquad \Delta G_{300\,°C} = -48.5\ \text{kJ/mol (eq. 2)}$$

Thus, the H_2S content in the desulphurized biogas should be kept as low as possible for catalytic conversion of biogas in order to achieve a long catalyst lifetime.

Catalytic methanisation is highly suited for energy storage and is driven by hydrogen (H_2) from renewable energy electrolysis. The CH_4 produced is easily stored in the natural gas grid. Much ongoing research is investigating the possibility of implementing catalytic methanisation at biogas plants [28–31]. However, so far only few demonstration plants have been reported [32,33]. The largest demonstration plant is the E-gas facility by Audi in Werlte, Germany [34], which operates with the off-gas from a nearby first generation upgrading biogas facility.

Chemoautotrophic Biogas Upgrading

In a biological upgrading approach, microorganisms use CO_2 as the carbon source and reduce it to biomethane. The energy input for this reduction can be provided by reduced compounds such as H_2, which provides electrons for the conversion. H_2 can be used by archaeal hydrogenotrophic methanogens, which converts it with CO_2 to methane. Hence, coupling excess electricity with biomethanation appears to be a very attractive solution.

The biological upgrading approach has several technological advantages compared to thermochemical-based technologies. One of the inherent advantages is that the process occurs at mild temperature conditions (in the range of 30 ºC to 60 ºC i.e. mesophilic or thermophilic) and close to atmospheric pressure. This impacts in a positive way not only with respect to technology safety but also towards the overall economy of biomethanation [35]. Moreover, the process is facilitated by hydrogenotrophic methanogens, which are abundant microorganisms found in biogas plants. Mixed cultures can be used to facilitate the conversion process, meaning sterile conditions are not required. The chemoautotrophic biogas upgrading methods have been validated at both laboratory and pilot scale.

Photosynthetic Biogas Upgrading

Another discussed approach is based on the symbiotic interactions between oxygenic photosynthetic, lithoautotrophic and heterotrophic microorganisms (i.e. microalgae and cyanobacteria). Today, these microorganisms represent the only biotechnology organisms capable of simultaneously removing multiple biogas pollutants as e.g. CO_2, H_2S, etc. [36]. This novel biogas upgrading biotechnology relies on photosynthetically driven fixation of CO_2, coupled with the removal of CO_2 along with other impurities with in the biogas. Apart from capturing CO_2, the produced algal biomass can be used for several other purposes. Moreover, nutrients (N, P) are captured [37,38]. Nevertheless, despite the obvious advantages, this approach still has several unsolved technical challenges and remains in the proof-of-concept phase. Several projects are currently trying to develop relevant upgrading technologies such as the EU Horizon 2020 funded projects INCOVER and URBIOFIN [39,40]. The efficiency and sustainability of these technologies still remain to be shown and especially, to be evaluated under industrial relevant conditions.

In addition to the above mentioned technologies, new emerging technologies are continuously appearing in the R&D literature. These include fermentative technologies where microorganisms are able to produce dicarboxylic acids by capturing of CO_2 along with the conversion of sugars, which provide the reducing equivalents. One very well developed approach is production of biosuccunic acid along with biogas upgrading [41]. Biosuccinic acid is a chemical platform, which has wide range of applications. Today, succinic acid is mainly produced from petrochemicals.

Syngas Conversion to Liquid Organic Molecules

Another second generation upgrading process would be the conversion of biogas to liquid organic molecules. The process may be divided into two steps: syngas production and synthesis of organic compounds, e.g. methanol. In the first step, the CH_4 and CO_2 in the biogas is reformed to carbon monoxide (CO) and H_2 in a combination of different reforming processes:
Steam reforming:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta G_{850\,°C} = -57.8\ \text{kJ/mol (eq. 3)}$$

and
Dry reforming:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta G_{850\,°C} = -58.8\ \text{kJ/mol (eq. 4)}$$

Olah and co-workers [42] have tested a similar process for methanol production from pure CH_4. Here, the authors combine steam and dry reforming in a 2:1 ratio in a single process called bi-reforming:

$$3CH_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H \qquad \Delta G_{850\,°C} = -174\ \text{kJ/mol (eq. 5)}$$

Bi-reforming yields syngas with the correct stoichiometric ratio for methanol production, although, it requires that the CH_4 to CO_2 ratio to be 3:1. Most biogas plants have a ratio of around 2:1 for the CH_4 to CO_2 ratio, which does not allow for a direct implementation of the bi-reforming process. Instead, at a 2:1 ratio of steam to dry reforming, the biogas composition is better suited for a 1:1 ratio of CH_4 to CO_2:

$$2CH_4 + CO_2 + H_2O \rightarrow 3CO + 5H_2 \qquad \Delta G_{850\,°C} = -117\ \text{kJ/mol (eq. 6)}$$

This process, termed *bio-reforming*, requires additional H_2 in order to obtain the correct stoichiometric ratio between CO and H_2. For methanol synthesis, the required CO:H_2 ratio is 1:2 [43].

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta G_{250\,°C} = 26.8\ \text{kJ/mol} \quad \text{(eq. 7)}$$

This will allow for energy storage, similar to the methanisation process, as the H_2 added to the synthesis could be produced by wind turbine or solar energy enabling green hydrogen formation through electrolysis.

Like the methanisation process, both steam and dry reforming uses a nickel catalyst [44]. Hence, deep upstream desulphurization is required, as also described for the catalytically methanisation above.

A liquid organic compound, such as methanol, is not only much easier to store as compared to upgraded CH_4, it also has a higher commercial value. Today, most of the methanol produced in the world is made from fossil fuel [45], although, biomethanol is already produced by gasification of biomass [46]. The list of applications for low-carbon footprint, organic compounds are many including fuel for airplanes, polymer production, formaldehyde synthesis, etc. [47–49].

Flexible Solution

Flexibility is essential for effective energy storage. Regularly turning the technology on and off is needed to follow the fluctuations of green electricity based on solar cells and wind turbines. Ideally, the storage system can switch from storing (i.e. using electricity) to producing electricity in much the same way as batteries or hydropower [50]. Second generation biogas upgrading has a different goal, since the main objective is to replace fossil fuels in hard-to-decarbonize applications.
Since biogas production is continuous, the application of the biogas should also be continuous. Nevertheless, not all second generation biogas upgrading technologies have this opportunity.
Catalytic methanisation favours continuous operation due to the applied temperatures and will need to shut down if the H_2 supply fluctuates or stops. The methanol production, however, opens up for much more flexible production.
As described above, to reach the correct stoichiometric composition of the syngas produced from biogas, additional H_2 is required. Should the H_2 supply stop, however, the methanol production would not stop, but simply produce less. Under the assumption that the production efficiency does not change, approximately 80% of the methanol production would remain. In the case of too little hydrogen inflow, the produced methanol would contain an additional amount of CO, which is not desired, and a gas cleaning system would need to be implemented if the methanol production plant was designed in this way. A benefit from continuous production of methanol is the ability to deliver according to contract even though no excess energy is available for hydrogen generation needed in order to reach the optimal CO:H_2 ratio is 1:2.
However, for better overall use of the carbon, a more complicated system could be implemented, where the excess carbon is stored. For storage, CO_2 would be preferred over CO, and thus a CO_2 capture system upstream of the reforming process may be the best solution. The stored CO_2 can then be blended-in with the biogas when storage of electricity is required to increase the methanol production as the CO_2 can react with H_2 directly to form CO in the reverse water gas shift reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta G_{250\,°C} = 19.5\ \text{kJ/mol} \quad \text{(eq. 8)}$$

Or reacted directly to form methanol [43]:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta G_{250\,°C} = 46.3\ \text{kJ/mol} \quad \text{(eq. 9)}$$

A second generation biogas upgrading system for methanol production designed according to these design guidelines would have three modes of operation (see Figure 2):

- **Normal mode**: The system upgrades all the carbon in the biogas to methanol by adding H_2 from electrolysis. Electricity is stored in the additional synthesized methanol.
- **Production mode**: Storing CO_2 for later use. The methanol production is approximately 80% of normal mode and no electricity is used or stored in the synthesized methanol.
- **Power mode**: Adding CO_2 from the gas storage into biogas for higher methanol yield. Electricity is stored in the additional synthesized methanol production. The methanol production is higher than when running in the normal mode.

This system could have a complete utilization of carbon, a continuous methanol production, and have flexibility in electricity consumption. The ultimate performance would be achieved when combining with additional CO_2 sources converting CO_2 into methanol instead of letting the CO_2 into the atmosphere.

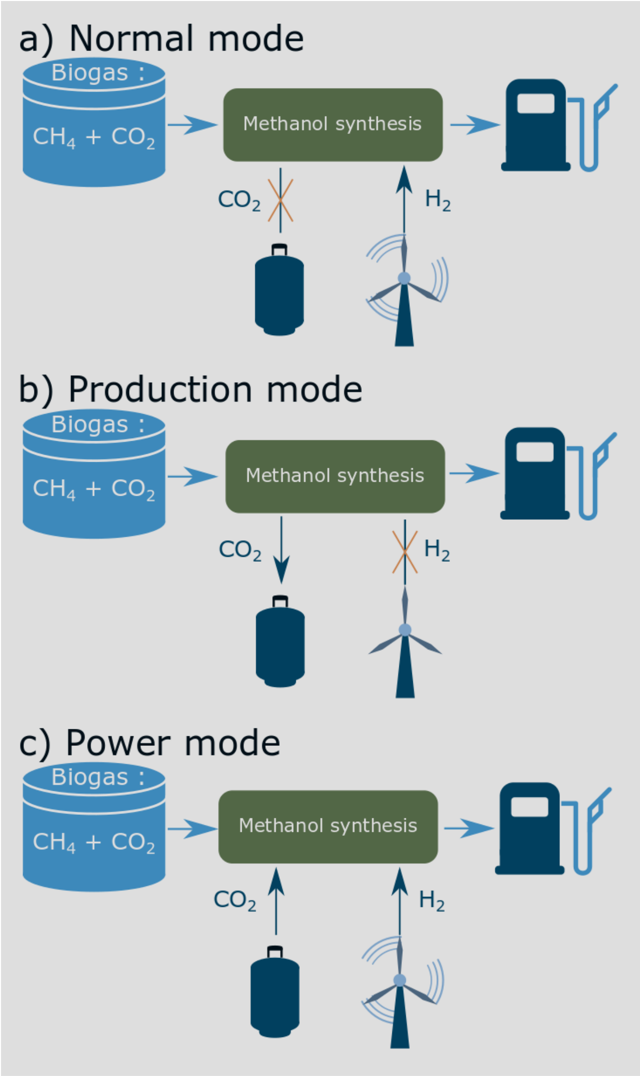

Figure 2: The three different operational modes of the methanol from biogas system. a) Normal operation which will convert the biogas to methanol requiring additional H_2 supplied by renewable electrolysis. Energy is stored. b) Production mode is entered when the electricity prices increase due to lack of renewable energy. Instead of adding H_2, CO_2 is removed from the biogas and stored while the production continues to operate at approximately 80% production when compared to normal mode without using electricity. c) Power mode where both CO_2 in the biogas and even stored CO_2 are converted into methanol. To increase the storing capacity of the system, additional CO_2 is added to the biogas, which requires additional H_2 for production of methanol. Overall, more energy is stored as methanol, as the production of methanol exceeds that of the normal operational mode.

Outlook

Biogas is an unusual renewable energy resource with several different aspects:

- Biogas is part of the waste management system. Biological waste can be used directly in the reactor.
- Biogas contributes to a lowering of the carbon footprint enabling green agricultural production.
- Biogas may even be considered a carbon capture technology, as much of the carbon ‘caught’ in the biogas reactor would otherwise have been emitted to the atmosphere.

Biogas has a lot of unused potential, and could prove central to the interconnected energy infrastructures of the future, as highlighted in Figure 3. Biogas is already a large industry that continues to grow. The upgrading technologies of today, i.e. first generation upgrading, are implemented at a commercial level. Since the market share is increasing, this indicates that the industry is open for new technologies.

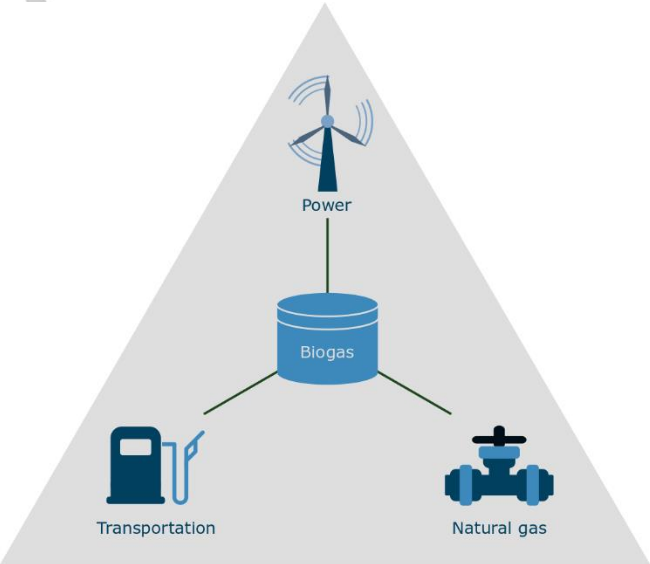

Figure 3: Biogas could be the nexus of three different energy infrastructures. When using biogas for storage of renewable energy, the carbon content allows for utilization both within the natural gas grid and as a versatile fuel in the transportation infrastructure

Using biogas as a medium for energy storage by adding H_2 (produced by (green) electrolysis), is receiving interest across Europe, and a few projects are currently researching this idea. The Sabatier reaction, methanol synthesis and biological conversion are today all in use at a commercial level, and although effort has to be made to adapt these technologies to biogas, it should be possible to implement within a relatively short timeframe.

We believe that a common terminology will help to promote research and development within second generation biogas upgrading. Furthermore, with many of the technologies required for implementation already available, we hope that with this increased promotion, the second generation upgrading could help to ease the green energy transition within 10 years, utilizing upgraded biogas in difficult-to-decarbonize industries**.**

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Keywords: Energy storage and conversion • Environmental chemistry • Biofuels • Sustainable chemistry • Biogas

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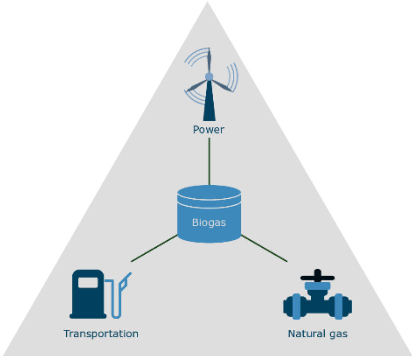
CONCEPT

We propose biogas as a carbon source for energy storage and argues for the introduction of the terminology 'first' and 'second' generation upgrading to distinguish between upgrading technologies.



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Page No. – Page No.

The Potential of Biogas; The Solution to Energy Storage