doi:10.20944/preprints202108.0463.v1

Negative CO_2 Emissions from Flexible Biofuel Synthesis: Concepts, Potentials, Technologies

Names of authors and affiliations:

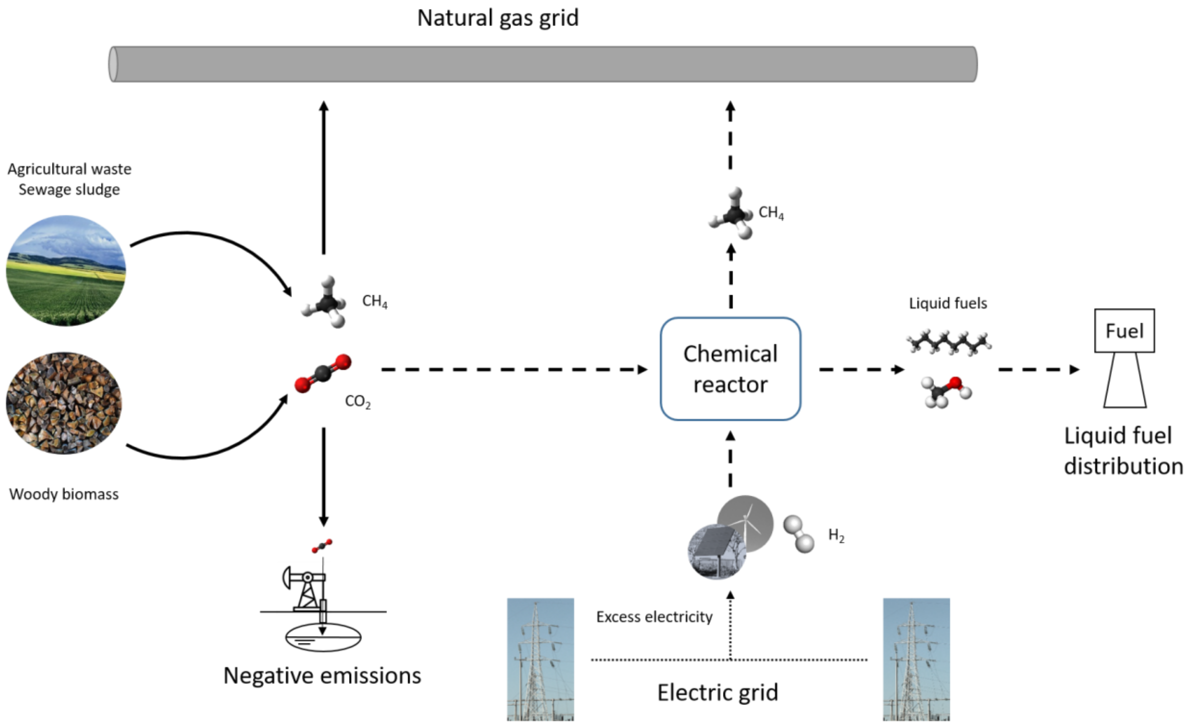
Emanuele Moioli*, Tilman Schildhauer

Energy and Environment Division, Paul Scherrer Institute, Forschungstrasse 111, Villigen Switzerland

Corresponding author

Name: Emanuele Moioli

Email address: Emanuele.moioli@psi.ch



Abstract

This review reports the available technologies for the flexible utilization of biomass towards negative CO_2 emissions and addresses the possibility to couple biogas production plants with the electrical grid converting excess electrical energy into storable chemical molecules. This changed mind-set towards biomass utilization can lead readily to the implementation of negative CO_2 emission along the entire bioenergy supply chain without limiting the potential for Power-to-X applications. First, the technologies for direct conversion of waste and wood into gaseous energy carriers are screened, to highlight the potential for the production of renewable fuels. Second, the processes for the removal of CO_2 from biogenic gas streams are analysed in terms of technological performance, cost and further potential for the CO_2 recovered. These technologies are the key to pre-combustion CO_2 capture and negative emissions. Third, the possibility of coupling biomass conversion and synthetic fuels production is explored, providing an overview on the technical maturity of the various energy storage processes. The flexible use of biomass can be an essential part of the future CO_2-free energy systems, as it can directly provide energy carriers all around the year and also large quantities of climate-neutral carbon for the production of synthetic fuels with renewable energy. In turn, when no additional renewable electricity is available, the CO_2 by-product from biofuel synthesis can be used for the negative emissions. This opens the way to an efficient strategy for the seasonal storage of electrical energy, realizing a carbon-neutral energy system coupled with the development of carbon-negative energy strategy.

Keywords: Power-to-X, Biomass, Biogas, renewable energy, energy storage

Highlights:

- Biomass is a key platform for the supply of CO_2
- Anaerobic digestion and gasification are the main technologies for biomass valorisation
- CO_2 produced can be captured and stored, enabling negative CO_2 emissions

- CO_2 can be used in chemicals production with renewable H_2, when available
- The two operation modes can flexibly adapt to the energy demand and offer

1. Introduction

The need to mitigate the climate change has lead to important efforts along the main lines of decreasing energy consumption, expanding the renewable electricity production (by e.g. photovoltaic systems, wind turbines and hydropower) and reducing the carbon footprint of energy carriers such as natural gas, Diesel fuel and gasoline. As not all greenhouse gas emissions can completely be avoided at resonable costs, meanwhile even negative CO_2 emissions are thought of.

For the defossilisation of energy carriers, often also referred to as decarbonisation, the carbon atoms in these hydrocarbons have to be from non-fossile origin, i.e. taken from biomass or from the air as CO_2 (referred to as direct air capture DAC) [1]. In case of DAC, hydrogen from renewable sources has to be added within the fuel synthesis to yield a renewable fuel; in case of biofuels, the addition of renewable H_2 is not always required but helps to increase the biofuel yield. This is due to the fact that biomass contains oxygen, besides carbon and hydrogen, while energy carriers contain no (natural gas, Diesel fuel, gasoline) or less oxygen (e.g. methanol). Without hydrogen addition, the oxygen has to leave the system as (biogenic) CO_2, while hydrogen addition favours the formation of water which allows a significant increase in the hydrocarbon yield [2].

Interestingly, capturing biogenic CO_2 and CO_2 from DAC and its subsequent injection into previous gas field like the Sleipner in Norway [3] are the two most important ways to create negative emissions with the aim to remove greenhouse gases from the atmosphere. Often it is susggested to achieve negative emissions based on the energetic use of biomass (also referred to as BECCS, Bioneenergy Carbon Capture and Sequestration) by capturing CO_2 from biomass combustion, for example from large wood-based boilers. Another frequently discussed approach is precombustion CCS of biomass, i.e. the gasification/reforming of biomass, followed by water gas shift reaction to produce the maximum hydrogen account and capture plus sequestration of the remaining CO_2 [4].

This review paper wants to highlight a third option for negative emissions. As discussed above, CO_2 is an inherent by-product from biofuel synthesis whose production is already included in the biofuel costs and efficiency [5]. For negative emissions, it has to be collected and transported to the sequestration sites, which is connected to less energy consumption and/or costs than the two BECCS concepts mentioned before or than CCS with direct air capture. The amounts of biogenic CO_2 that can be collected this way are lower than the ones from BECCS at biomass boilers. In fact, the biogenic CO_2 should be used in times of electricity over-production as carbon feedstock within Power-to-Hydrocarbons processes allowing for seasonal energy storage and sector coupling. For this reason, we can quantify the amount of CO_2 available in about 20 to 40 % of the original total carbon content of the biomass [4]. However, despite limited, this amount of CO_2 is significant for the development of a CO_2 negative energy strategy, thanks to the easiness of separation and handling of this fraction. The technologies for this least-cost negative emissions in times when electricity is scarce (e.g. in winter) are numerous and will be explored within this review paper.

In fact, a study reviewing the currently available technologies for the flexible utilization of biomass towards enabling negative CO_2 emissions is currently lacking in literature. Hence, this review is devoted to the description and analysis of the available technologies and the potential for the flexible integration of bioenergy, Power-to-Hydrocarbon processes and negative emissions. Additionally, we show the potential for switching between two operation modes: valorisation of the CO_2 waste streams (energy storage) and CO_2 capture and permanent storage (negative emissions). The switch between these two operation modes increases the flexibility of the system, adapting to the scattering energy market. The potential for flexible biomass utilisation is significant and largely unexplored. For example, in a small country like Switzerland, it is calculated that more than 40 PJ of renewable biomass resources are still available for energetic exploitation [6].

The structure of the review is represented in figure 1. After this introduction, section 2 is devoted to the description of the existing processes for the recovery of agricultural waste and for the energetic valorisation of woody biomass. For what concerns the fermentation of agricultural and urban waste and for the valorisation of sewage sludge, we analyse the product distribution, the need for gas cleaning and the economic performance in terms of cost of the biogas produced. Concerning the technologies for the gasification of woody biomass, we describe the various configurations of gasifiers whose operation has been demonstrated, we analyse the available options for gas cleaning and the possible configurations of the post-treatment train according to the desired product distribution.

In section 3, we analyse the existing technologies for the removal of CO_2 from biogas streams. These form the first pillar of the flexible use of biomass, because they allow both the production of biomethane (i.e. a gas mixture composed of sufficient methane for the direct injection in the natural gas grid) and the recovery of biogenic CO_2, to use in further processes (CCS or CCU) towards negative emissions. We compare pros and cons of the technologies and provide the cost estimation of these separation techniques.

Section 4 concerns the direct methanation of biogas, the technology for the valorisation of biogenic CO_2 closest to full maturity. We analyse the reactors available and briefly compare the biological and thermo-catalytic methanation. We report the existent economic analysis and the potential for further implementation of the technology in the flexible use of biomass.

Finally, section 5 is devoted to a brief screening of the available synthesis routes to convert biogenic CO_2 into valuable products in the presence of renewable H_2. In this case, we describe the research needs for these processes (with special focus on methanol and hydrocarbons) and give an outlook to the potential for commercialization of the flexible solutions for the use of biomass in the production of liquid products.

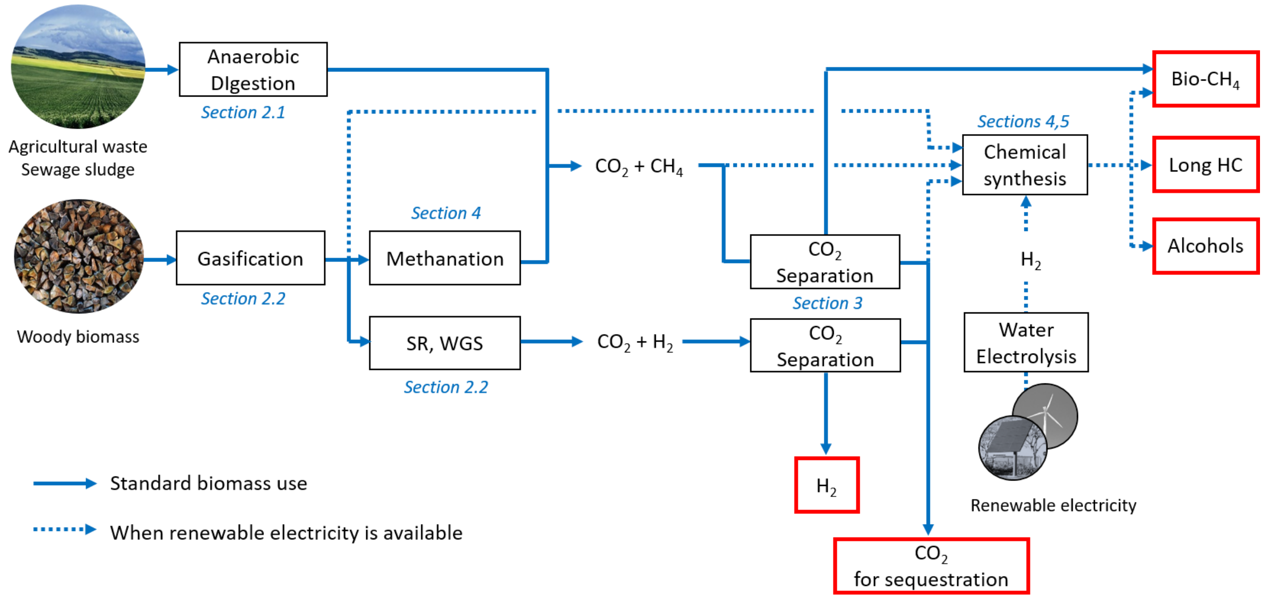


Figure 1 Structure of the review

2. Processes for treatment of agricultural waste and wood

2.1. Fermentation of agricultural residues, organic urban waste and sewage sludge

For the energetic valorisation of agricultural residues, organic urban waste and sewage sludge (originated from wastewater treatment plants), the most common technology is the anaerobic digestion to produce biogas. In this technology, microorganisms ferment the organic matter into methane and other molecules. Various factors affect the yield and selectivity of the process, including pH, temperature, C/N ratio and hydraulic retention time [7]. The process is performed in controlled chambers, requiring low investment cost and generating an economic output from a waste that otherwise should be treated [8]. The microorganisms must be selected according to the feedstock and kept in appropriate conditions, so that they can correctly operate in the biogas plant. Three different types of feedstock can be distinguished, according to the water content in the biomass: wet, semi-dry and dry. The wet process is operated with the residuals of wastewater treatment plants, due to the high water content (content of solids normally below 10 %) [8]. The semi-dry technology is employed with municipal organic waste, which shows a content of solids up to 20 %. The dry technology is used for a solid fraction above 20 % [9,10]. However, the dry technology is more favourable, thanks to the lower amount of water required, which results in a lower cost of the production due to lower size of the equipment. Additionally, it was found that the water content influences the activity of the methanogenic organisms [10,11]. Over the last few years, the number of commercially available substrates for the production of biogas has increased considerably, optimizing the utilisation of the wastes and making it possible to make this process economically attractive. Only considering Europe, we can already account for several hundreds of biogas plants [12].

The composition of the biogas produced varies significantly with the biomass used. Examples of the amount of methane contained in the biogas from various sources are reported in table 1. In all the cases, the methane amount is above 50 %, most commonly about 60 %. The remaining gas is mainly CO_2, which has to be further removed from the gas stream with the technologies reported in section 3 (biogas upgrading). This CO_2 content of about 40 % is readily available to enable negative emissions and is therefore a key for a cheap introduction of the BECCS strategies.

Table 1 methane content in the biogas and yield of biogas from various sources (elaborated from [8]*). DM=Dry Matter.*

Organic source	Methane content in biogas [%]	Yield of biogas production (dm^3/kg DM)	Ref.
Agro-food industry waste	65-70	400-700	[13]
Sewadge sludge	60-75	200-300	[14]
Municipal green waste	50-60	350-450	[13]

Apart from CO_2, the biogas can contain several other contaminants that must be eliminated to ensure a safe utilization of bioenergy. These contaminants can be removed with primary (addition of elements to the substrate to avoid production of these contaminants) or secondary measures (removal of contaminants from the biogas). The most relevant impurities are nitrogen, oxygen, water, hydrogen sulphide (H_2S) and siloxanes [15]. H_2S and siloxanes are particularly dangerous for the successive post-treatment of biogas. H_2S causes corrosion of the metal parts of energy converters and generates harmful compounds in exhaust gases [16]. Siloxanes decompose to microcrystalline silica (SiO_2) which generates dangerous deposits on the inner surfaces of energy converting units (such as turbine blades, cylinder heads, heat exchanger walls and so on), causing abrasion in the moving parts [17]. In primary measures, the formation of H_2S is prevented by adding appropriate materials which can precipitate sulphur. These include: dosing of O_2/air in the system (to form S and H_2O) and the addition of $FeCl_2$ (which reacts with H_2S to form solid FeS) [18,19]. Secondary measures include the adsorption of H_2S on iron oxydes/hydroxydes or on activated carbons [15,20]. These materials are also effective in removing siloxanes from the biogas [16].

2.2. Gasification of woody biomass

2.2.1. General aspects

The gasification of woody biomass is a thermal treatment of the biomass that generates a product gas containing mainly CO, CO_2, H_2, CH_4 and higher hydrocarbons. Additionally, the gasification product gas may contain several impurities, such as tars, hydrogen sulphide, organic sulphur species, ammonia, according to the nature of the biomass used [21]. These impurities are eliminated with hot or cold gas cleaning technologies, according to the final use of the gasification products [22]. As the C/O/H ratio in the biomass is usually not favourable for the production of fuels, an additional H_2 source is required, to improve the characteristics of the product gas. For this reason, H_2O is often added in the gasification reactor. However, the reaction of biomass with H_2O is endothermic, so that part of the biomass must be burned to provide the required heat. This generates additional CO_2 emissions that can be avoided by post-combustion CO_2 capture. The amount of CO_2 produced in this section account for about 30 % of the original carbon content of the woody biomass [4].

The product distribution is strongly depending on the reaction conditions, especially temperature and pressure. Thermodynamic equilibrium calculations show that methane production is favoured by lower temperature and high pressure ($T<600$ ˚C and $P>10$ bar). The concentration of hydrogen and carbon monoxide increases with temperature; this leads to a rise of the endothermal nature of the process with temperature. For this reason, the production of hydrogen and carbon monoxide from biomass requires heat supply at high temperature [23,24]. Even though higher hydrocarbons are almost absent according to thermodynamic calculations, they are produced in real gasifier operation, because equilibrium is not fully reached. Additionally, in many gasifier types, a significant amount of material remains unconverted and it is collected in the ashes in form of char. This material can be combusted to obtain the heat required for gasification (as performed, for example, in the dual bed gasifier).

According to the desired final product (e.g. SNG or H_2) various technologies can be employed for biomass gasification. However, as different conflicting objectives have to be considered (e.g. high methane yield, but low higher hydrocarbon yield) the interplay of the various parameters tends to compensate. This is, for example, the case of pressure, as pressurized operation favours the formation of methane, but makes the handling of the feedstock more challenging. Therefore, from an exergy perspective, there is no evident advantage in operating the gasification vessel at high pressure, because the advantages of compression are compensated by increased energy demand in the downstream processing [25]. Following these considerations, no technology can be considered as the optimal gasification, but the optimization must be conducted according to the specific process framework. For this reason, the main technologies are here presented and analysed individually.

Table 2 Typical product gas of biomass gasification in the various technologies analysed

	Concentration [mol. %]					
Technology	H_2	CH_4	CO	CO_2	C_{2+}	Ref.
Entrained flow	35	-	60	5	-	[26]
BFB	19	17	26	37	1	[27]
(Oxy-)SER	70	15	4	8	3	[28]
DFB	39	10	23	25	3	[29]

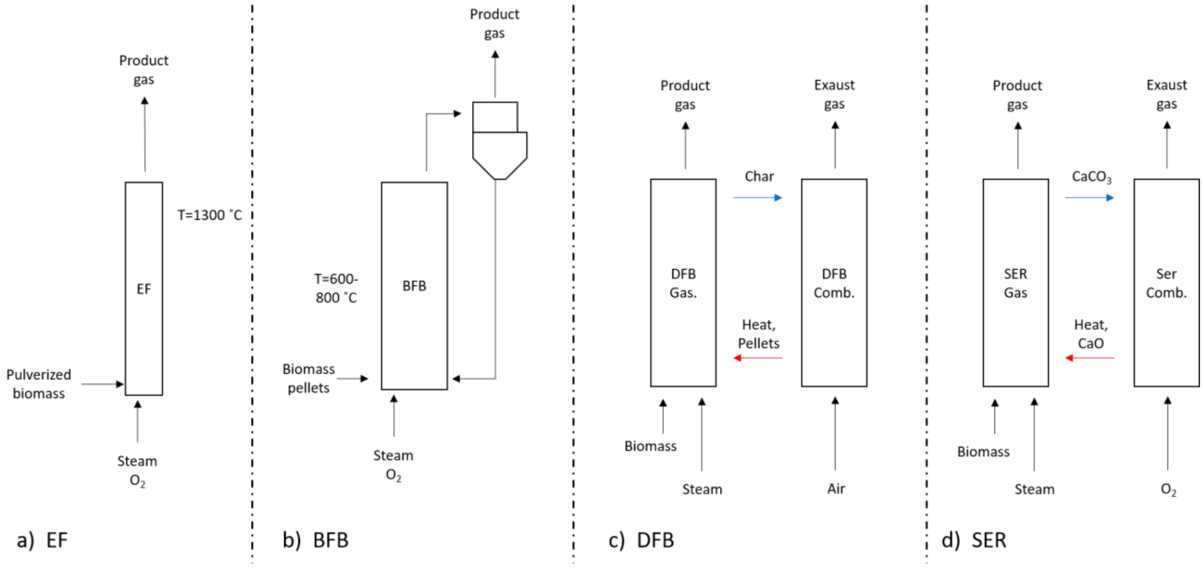


Figure 2 Detail of the four gasification technologies considered

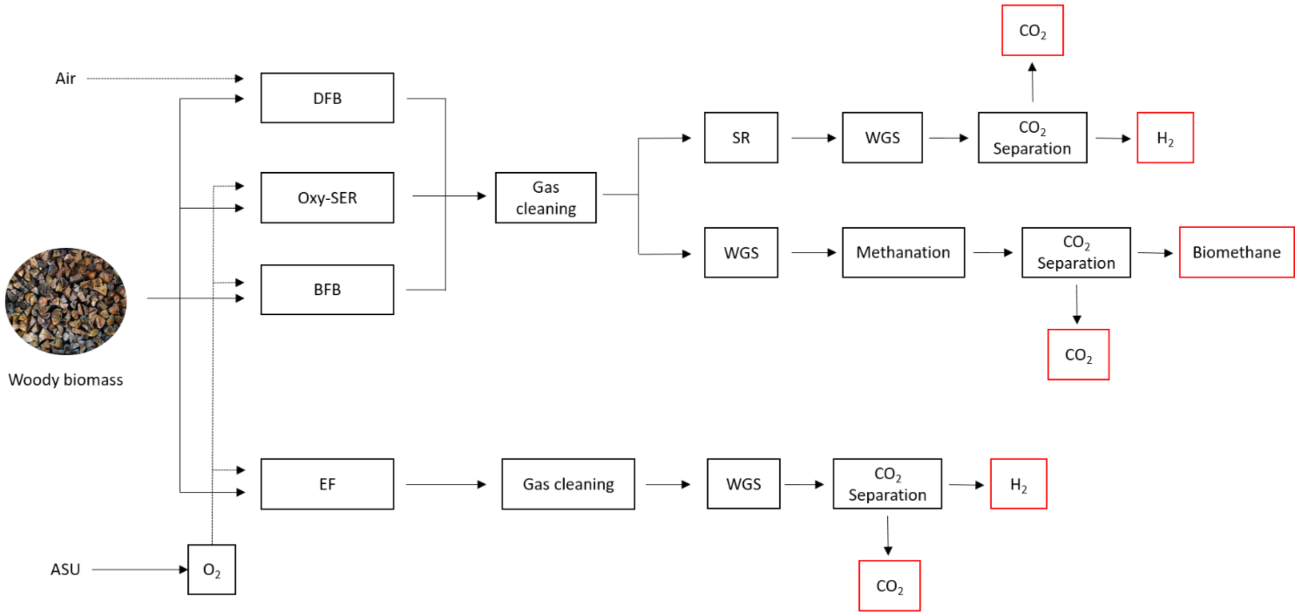


Figure 3 Overview of the process chains for biomass gasification technologies

2.2.2. Available technologies

The gasifiers that are employed in the treatment of woody biomass can be classified into three categories: entrained flow, direct fluidized bed and indirect fluidized bed gasification. A process flow diagram of the technologies is shown in figure 2, while the whole gas purification trains are sketched in figure 3. The representative product gas composition after the four gasification technologies is reported in table 2.

Entrained flow gasification. The main characteristic of entrained flow gasification is the rapid transport (entrainment) of the feedstock by the gasification agent, together with the product gas. In this way, the residence time is low (below 5 s), which requires high reaction temperature (usually above 1300 ˚C) [21]. Thanks to the high temperature, the production of hydrocarbons is avoided and the product gas is mainly composed of H_2, CO and steam. Due to the high temperature required, the gasification agent is usually pure oxygen, supplied from an air separation unit (ASU) [30]. Additionally, avoiding the presence of nitrogen, the purification of products is facilitated. However, the requirement for the ASU and for the pre-treatment (pulverisation) of the biomass increase the energy demand and the complexity of the system. A standard product gas composition is as follows (in mol %) [26]: H_2=35-40 %, CO= 55-60

%, CO_2=0-5 %. This product composition facilitates the downstream processing towards bio-H_2, as there is no need for the endothermic steam methane reforming. The production of H_2 is thus enhanced by a WGS reactor, which can be operated after the gas cleaning step. The remaining gas is composed of H_2 and CO_2, which can be separated following the processes described in section 3. Alternatively, if the desired product is bio-CH_4, it is possible to operate a methanation reactor after the gas cleaning and a first WGS step, converting all the H_2 into CH_4. The product stream is, in this case, a mixture of CH_4 and CO_2, to be purified prior to injection to the gas grid or directly used for CHP production.

Entrained flow gasifiers exist at large scale and are provided by various suppliers [23]. The technology was principally developed for the conversion of coal in integrated gasification combined cycle (IGCC) plants. For what concerns biomass gasification, entrained flow gasification plants have been developed in the BioTFuel [31] and in the BioLiq® [32] projects. This technology is currently employed for the production of methanol/DME or FT fuels, thanks to the production of a suitable CO/H_2 mixture. The use of entrained gasifiers is less common in the framework of SNG production, due to the suppression of methane formation in the gasification chamber.

Direct fluidized bed gasification. The direct fluidized bed gasification the biomass consist of an unit where the biomass reacts with steam and oxygen in the presence of bed material, which is used to maintain an even temperature distribution in the reactor and to improve fuel mixing. There are two possible configurations of the reactor: bubbling fluidized bed or circulating bed. In the former, the particles remain in the reactor, while in the latter the entrained particles are separated from the product gas by a cyclone and returned to the reactor via a return leg. The product gas composition is reported in table 2 (BFB section). As the amount of methane is significant, production of bio-H_2 is challenging with this gasifier type. In fact, methane must be reformed with steam at high temperature in an endothermic reaction. This creates difficulties in the integration with the gas cleaning [33], which has to be operated at lower temperature than the steam reformer. Therefore, the process chain to bio-H_2 can be implemented only if external heat is available (e.g. from burning of tail gases). The process chain towards bio-CH_4 is instead less challenging, as the reactions to convert CO and H_2 into CH_4 can be operated at lower temperature than the gas cleaning section. In this case, after the gas cleaning, the CO is passed over a methanation/WGS catalyst (eventually after addition of steam) to be converted into methane, according to the available amount of H_2. The result is a CH_4/CO_2 stream to be further employed for energy production and/or energy storage.

The bubbling fluidized bed technology is commercially available. Winkler gasification is in operation in various applications since the 1970s [34,35], including the production of syngas for the methanol synthesis [36] and a biomass to methanol project [37]. Further examples of this technology are the Foster Wheeler gasifier [38] and the AndritzCarbona/GTI plant [39,40].

Indirect fluidized bed gasification. The indirect fluidized bed gasification separates the biomass combustion section (exothermic reaction) and the biomass gasification section (endothermic reaction) in two different reactors. In large-scale operation (>50 MW_{th}), the most common technology is the circulating bed reactor and the biomass is used as a heat transfer medium between the two sections. In these plants, the two reactors are interdependent and self-adapting. In fact, a decrease in the temperature causes the production of a larger amount of char, resulting in a larger heat production in the combustion chamber and vice versa. The main advantage of this system is the possibility of obtaining a nitrogen-free product gas without, in principle, the need for pure oxygen supply. This significantly reduces the investment costs, as the ASU is not necessary. One example of this technology is the dual fluidized bed gasifier (DFB) [29,41,42]. In this technology, the gasification reactor is a bubbling fluidized bed and it is operated with steam. The combustion reactor is, instead, a fast-fluidized bed reactor operated with air. The separation between wood gas from gasification and flue gas from combustion is ensured by fluidized loop seals. The bed material is usually composed of olivine, which is a good heat carrier and catalyses well the gasification reactions [43]. The typical composition of the product gas is reported in table 2 (DFB). The amount of H_2 present is doubled than in the case of the BFB, making it more suitable for further treatment of the gas towards hydrocarbons. The H_2:CO ratio of approximately 2:1 sets this gas in the correct range for the FT synthesis. Direct bio-H_2 production is instead not favoured due to the presence of 10% CH_4 that must be reformed at high temperature, as in the case of BFB. The main drawback of the DFB as a bioenergy production plant is the impossibility to capture all the CO_2 produced due to the combustion with air. This causes the emission of ca. 1/3 of the C-content of the biomass as CO_2 [28]. The first pilot plant for the DFB technology was installed in Güssing, Austria [29], with a dimension of 8 MW_{th}. The same concept was used for a further demonstration of a 1 MW bio-SNG production [44]. In this case, the chemical efficiency biomass-to-SNG reached a value of 66%. A further demonstration of the DFB technology was provided by the GoBiGas plant in Sweden [45]. Here, a production of 20 MW of SNG from forest residues is operated. A special type of DFB gasifier is the MILENA gasifier, where combustor and reformer are included in the same vessel [46]. This increases the cold gas efficiency, but also lowers the residence time due to the use of a riser reactor. This technology was utilized to produce bio-SNG in the gasification of 12 MW_{th} of waste wood.

Sorption enhanced reforming. The sorption enhanced reforming (SER) is a special case of indirect fluidized bed gasification. This reactor type uses CaO containing bed material, which contributes to the in-situ capture of CO_2. This is performed via the carbonation of CaO in the reaction:

$$CaO + CO_2 \leftrightarrow CaCO_3 \qquad \Delta H_0^R = -179\ kJ/mol \tag{1}$$

This reaction is highly exothermic and thus enhances the heat supply, while shifting the thermodynamic equilibrium of the WGS reaction. However, in order to complete the

doi:10.20944/preprints202108.0463.v1

carbonation reaction, lower temperature and longer residence time than the standard gasification are required. Additionally, the spent $CaCO_3$ must be regenerated at high temperature ($T > 900$ ˚C) in the reverse reaction (1), reducing the chemical energy input. For the SER gasifier, the energy efficiency is thus reduced to ca. 37 % [23]. On the base of all these phenomena, the product gas contains a large amount of H_2, while most of the CO_2 (ca. 60 % of the original C in the biomass) goes to the flow gas of the combustion chamber [28,47,48]. A significant amount of CH_4 (ca. 15% v./v.) is also present, due to the low gasification temperature. The fractions of CO and CO_2 are instead low. Due to this, the SER is particularly suitable for the production of bio-H_2, since no large treatment units are necessary (in particular no big shift reactor is required). Furthermore, an appropriate CCS strategy can be applied to the combustor, especially if this is operated in oxy-combustion.

The SER technology was validated in Güssing (8 MW_{th}) [49], but no larger demonstration units have been built so far.

2.2.3. Implementation

As observed in section 2.2.2, according to the technology selected, it is possible to substantially modify the product distribution in terms of CH_4, H_2, CO and CO_2. The downstream processes can modify this ratio, but with the drawback of higher installation costs and higher complexity of the system. In general, when H_2 is the target product, the quantity of methane in the gasifier outlet should be minimized. The conversion of CH_4 into H_2 by steam reforming (MSR) is the most challenging operation, as the reaction is strongly endothermic and requires high temperature due to the thermodynamic equilibrium. The operation of this reforming reactor directly at the gasifier outlet is not possible due to the presence of impurities in the gas stream, which would quickly deactivate the catalyst. These impurities must be removed at lower temperature than the MSR reactor ($T < 800$ ˚C), requiring re-heating of the gas after cleaning [50]. For this reason, the MSR unit can be economically operated only if high temperature heat is available at low cost (e.g. from a SOFC). Therefore, the EF or SER are the choice reactors for the production of bio-H_2. If the target molecule is bio-CH_4, the technological solution results less challenging, as the reactions to produce CH_4 from H_2, CO and CO_2 are exothermic and can be operated at lower temperature. This means that the product gas from the gasification can be first cleaned from the impurities and then reformed to bio-CH_4. The WGS reaction can be operated in two steps, at high and low temperature. The first step is operated over a Fe-Cr-based catalyst, which is resistant to sulphur poisoning and can thus be placed before the low-temperature desulphurisation [51,52]. After removal of the S-species, the final low-temperature WGS (over Cu/ZnO) and the CO/CO_2 methanation (over Ni) steps are performed. In these last reactors, H_2 from renewable sources can be added to enhance the bio-CH_4 production, creating a flexible use of the biomass. This latter possibility will be explored in detail in section 4. In general, we can conclude that the BFB and DFB are the optimal choice for bio-CH_4 production. The technologies here presented can be profitable only at large scale, due to the need for process integration and optimization of the heat exchange [5]. For this reason, a minimal size of the processes has to be reached to provide a competitive internal rate of return (IRR) for the investment [53]. However, the collection of large quantities of woody biomass can be challenging and require large transportation facilities, which can be relatively expensive [54]. Some solutions are being developed to avoid this problems, including the intermediate transformation of biomass in a liquid product (bio-oil) [54–56]. Alternatively, the development of more effective processes in terms of optimization of the dimensions of the various parts and in the operating temperature of the gas cleaning section could reduce the minimal size required for this type of plants [5,57].

3. Processes for CO_2 separation from biogas streams

3.1. Available technologies

The main inert component in the raw biogas is CO_2. As the removal of this component has different requirements than the elimination of other contaminants, the process is often referred to as ‘biogas upgrading’, while the removal of other components is called ‘biogas cleaning’ [58]. Biogas upgrading is a key technology towards the prompt implementation of negative CO_2 emissions, as the CO_2 separation is anyway performed to valorise the methane from biogas and the resulting CO_2 can be compressed and stored with relatively low effort.

Table 3 characteristics of the main biogas upgrading technologies (analysis of data from [59,60]*). RT=room temperature*

	Water scrubber	**Pressure swing adsorption**	**Chemical absorption**	**Membrane**
Electricity demand [kWh/Nm$^3_{BG}$]	0.2-0.3	0.2-0.25	0.15	0.25
Operation temperature [˚C]	RT	RT	120-160	RT
Pressure (barg)	5-10	4-7	0.1	5-10
Methane recovery (%)	98	96	99.96	80-99.5
Methane content in upgraded gas (mol %)	>97	>96	>99	>95
Demand for chemicals	no	no	Yes	no
Operating cost (€/Nm$^3_{CH4}$)	0.13	0.25	0.17-0.28	0.12-0.22
Capital cost (€/Nm$^3_{Biogas}$/h)	2500-5000	1500-3000	1500-3000	2000-6000
Market share (%)	44	21	22	10
References	[59,61–63]	[59,62,64,65]	[59,62,65,66]	[59,66–68]

Several different technologies for biogas upgrading are currently available. CO_2 must be removed to obtain a product with adequate heating value (HHV) and to avoid the formation of dry ice upon compression of the biogas [59]. The goal of the project is thus to have a product which can substitute natural gas and be injected in the grid or used in internal combustion engines (ICE). The required purity of biomethane changes country by country. However, in almost all the countries, values of CO_2 above 5 % are not allowed [69]. The number of biogas installations with upgrading units has increased importantly over the last few years. Four main technologies are applied: water scrubbing, chemical absorption, pressure swing adsorption

(PSA) and membranes. In this section, we will analyse and compare these technologies, whose principle of operation is summarized in figure 4.

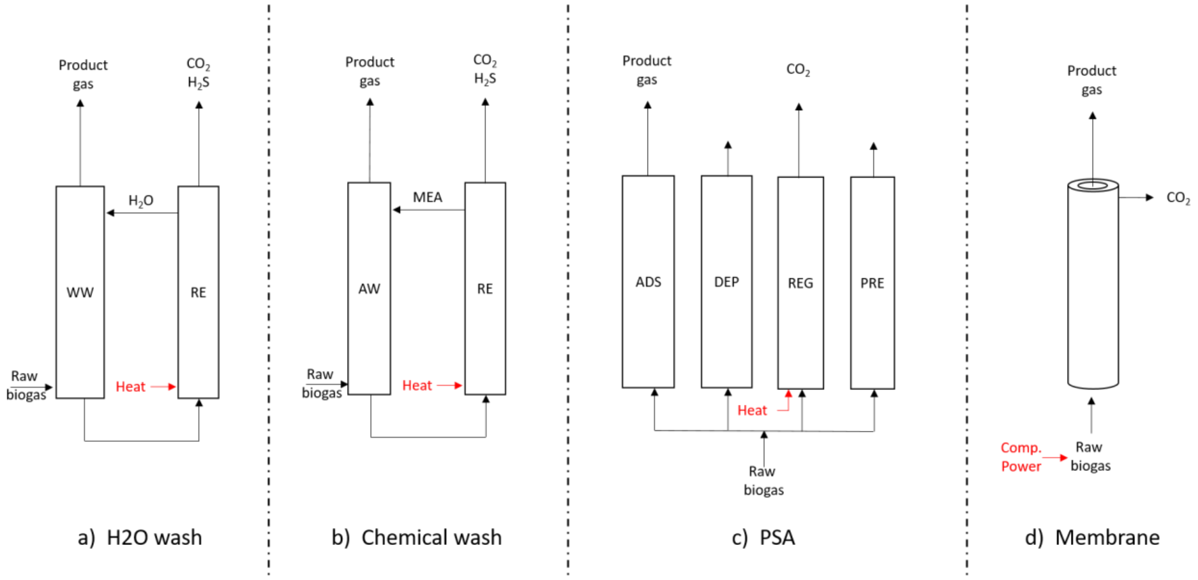


Figure 4 working principle of the four main biogas upgrading technologies (WS= wash column, RE=regeneration, ADS=adsorption, DEP=depressurisation, REG=regeneration, PRE=pressurisation).

Water scrubbing. The simplest way to treat biogas is by water scrubbing. In this technology, the different solubility of CO_2 and CH_4 in water is employed to purify the biogas. In fact, the water solubility of CO_2 is 26 times higher than CH_4 (at 25 ˚C). It is noteworthy to observe that H_2S is also absorbed with CO_2 [70]. This limits the applicability of the system, as the absorbed H_2S decreases the pH of the solution and thus also the solubility of CO_2 [66]. The efficiency of the system is between 80-90 % at 10-15 ˚C [71]. An increase of the temperature is detrimental for the performance of the system. The operation is performed in a pressurized vessel (usually 10-20 bar) where water is introduced from the top of the equipment and the biogas is fed from the bottom. The column is usually filled with packing material to increase the area for the mass transfer. The final purity of methane is often above 95 %. Water is regenerated in an appropriate column, by reduction of the pressure to 2-4 bar. The gas resulting from regeneration is composed of ca. 80 % CO_2 and 20 % CH_4 and can therefore be further treated for the recovery of the remaining CH_4 [72]. The amount of water required for this operation is high (0.1-0.2 m^3H_2O/Nm^3_{Biogas}) [62] and the plant can be operated in single pass (the water is released after regeneration) or with recycle (water is used several times in the scrubber) [61]. The methane losses are around 2 % [63], while the energy requirements are mainly due to gas compression, water pumping and regeneration. The capital costs for installation range from 2500-5000 €/Nm^3/h for plants with a capacity between 100-500 Nm^3/h [62,63]. Currently, about 40 % of the biogas plants have a water scrubber installed [59,73].

Chemical scrubbing. In chemical scrubbing, CO_2 is removed from the biogas by chemical reaction with appropriate components. The operation principle is similar to the water scrubbing, but the performance is improved, thanks to the use of materials tailored for CO_2 absorption (high CO_2 solubility) [74]. Typically, amines are used for this reaction and monoethanolamine (MEA) is the most employed compound, due to its high selectivity and high absorption capacity, together with low cost [75]. Several other mono- di- and tri-ethanolamines, as well as sterically hindered amines, are also used for biogas upgrading [76]. Alkali salts are also good CO_2 sorbents, but the slow reaction rate and the difficulties in regeneration limits their application in biogas upgrading [61].

The chemical scrubbing system is composed of two vessels, for absorption and regeneration. The absorption column is usually a packed bed column, where the risk of clogging is limited by the high pH of the chemical solution [58]. The biogas is introduced from the bottom of the column and contacted in counter-current with the sorbent. The temperature of the absorber increases during the operation (generally from 20 to 40-50 ˚C), due to the exothermic reaction [63]. The process takes place at low pressure (1-2 bar). The spent sorbent solution, removed from the bottom of the column, is regenerated in a stripping unit, with a reboiler providing the required heat for the endothermic regeneration reaction [63]. The large need of heat for regeneration is one of the main drawback of the technology, limiting the market share of chemical scrubbing to ca. 22% [59,73].

The performance of the technology is excellent, producing biomethane with concentration above 99%. The methane losses are minimized by its low solubility in the organic solution (loss below 0.1 %) [59]. The investment cost for the realization of a chemical scrubber range from 1500 to 3000 €/Nm^3/h, with the lower value being for a plant with 1800 Nm^3/h capacity. The costs of chemicals are marginal, while the energy required for gas compression and liquid pumping is in the range 0.12-0.15 kWh/Nm^3. The main operating costs are related to amine regeneration, with 0.55 kWh/Nm^3 [62,65,66].

Pressure swing adsorption. The pressure swing adsorption (PSA) is a technology involving the selective adsorption of specific components on a material. When the material is filled with the component to remove, the pressure of the system is modified, so that this latter is removed and the surface can be used again for adsorption. The sorbent is linked to the gaseous component by physical or van der Waals forces [64]. PSA needs a cyclical operation, characterized by periodical loading and regeneration of the sorbent. To obtain a continuous operation, four different units are necessary (figure 4d). These operate cyclically the four phases [59,62]:

1. Adsorption: biogas at 6-8 bar is fed into the vessel, until the material is filled with CO_2.
2. Depressurisation: the vessel is brought to low temperature.
3. Regeneration: the unit is purged at ambient pressure or in vacuum, using part of the product CH_4 to remove CO_2
4. Pressurisation: the pressure of the vessel is increased to prepare for a new cycle.

The materials used for PSA are mainly zeolites or carbon-based adsorbents. Recently, also metal organic frameworks (MOF) and silico-aluminophosphate (SAPO) sorbents have been tested for the process [64,77].

The biogas upgrading with PSA requires the previous separation of H_2S, siloxane and moisture, as these are poisons for the sorbent. The methane recovery rate for PSA is relatively low, because significant amount of CH_4 is lost in the off-gas [63]. This correspond, in the best cases, to a CH_4 recovery of 96 %. For this reason and for the complexity in the construction, the market share of PSA is about 20 % [73].

The capital cost of a PSA unit is between 1500-3000 €/Nm^3/h, the lower value being for a plant with 2000 Nm^3/h capacity [62,65]. The electricity cost (for compression of biogas) is in the range of 0.24-0.6 kWh/Nm^3 [78].

Membrane separation. The membrane separation exploits the properties of semi-permeable materials to selectively isolate the various components. The membranes used in this field preferentially retain CH_4 and separate CO_2 in the permeate stream. The CO_2/CH_4 selectivity can be up to 1000/1 [68]. Membranes for biogas separation are essentially of three types: polymeric, inorganic and mixed matrix (MMMs).

Polymeric membranes (such as polysulphone (PsF), polyimide (PI), cellulose acetate (CA) and polycarbonate (PC)) possess high permeability, and excellent mechanical and thermal strength [67]. CA and PI membranes are the preferred solutions for biogas upgrading. CAs are cheap and stable; their main limitation is the susceptibility to plasticization (with a plasticization pressure of 8 bar). PIs show high selectivity and permeability, as well as mechanical stability. Their plasticization pressure is 17 bar [59].

Inorganic membranes possess a higher mechanical strength, thermal and chemical stability than polymeric membranes, but they are difficult to manufacture, owing to high cost [59]. MMMs aim at combining the advantages of the two, forming a continuous phase with dispersed inorganic molecules [79].

Operation of membrane separation often involves the use of pressurized biogas up to 20-40 bar. The flow of biogas through the membrane results in the separation of a CH_4 rich retentate and a CO_2 rich permeate (figure 4d). This is the main drawback of the technology, as a fraction of CH_4 passes the membrane and remains in the CO_2 side. This leads to a methane recovery of

92 % per pass. In order to achieve the required gas quality, multistage membranes are employed [67]. With a multistage membrane system, 80 to 99.5 % methane recovery is possible, with lower investment and operating cost compared to single stage membranes [80]. The investment costs related to membrane installation are in the range 2000-6000 €/Nm^3/h, with the former value for applications above 1000 Nm^3/h [67]. the operating costs involve mainly the membrane replacement (in average every 5 years) and the compression of biogas (0.2-0.4 kWh/Nm^3) [66]. The market share of biogas upgrading with membrane is currently ca. 10% [73].

3.2.Comparison of the technologies

As observed in the previous section, no technology shows a superior performance over the others. The water scrubbing currently has a dominant position on the market, due to the simplicity in using water as cleaning agent. However, this technology requires large plants, treatment of large amount of water and an important investment cost. This makes it particularly suitable for large biogas plants, which also correspond to the size where valorization of biogas into biomethane is particularly profitable. In fact, according to factors like the proximity of gas network and electricity grid, it is possible to find a critical capacity threshold above which the production of biomethane is favorable over other valorization techniques, such as CHP [81,82]. The combination of these two factors (suitability for big plants and profitability of large biomethane production) is the reason of the success of this technology. The alternative technologies here described can instead contribute to the development of biomethane production at lower scale, thanks to the lower investment costs. In this sense, especially for the low investment technologies chemical absorption and PSA, the market share can increase in the upcoming years, opening the way for the conversion of smaller biogas plants into biomethane facilities. Different is the case of membranes, which, despite a high investment cost, can find applications in small-scale plants, thanks to their modularity and ease of installation. In any case, in future, the biogas upgrading technologies are going to play a role also as supplier of biogenic CO_2 for negative emission technologies, eventually including CO_2 storage and distribution. For this reason, a rising important characteristic of the biogas upgrading technologies is the possibility to combine them with synthetic fuels production units, which are discussed in the following sections.

4. Processes for the flexible use of biomass in the production of synthetic natural gas

4.1.Basic principles of CO_2 methanation

The most mature technology in the field of synthetic fuel production from CO_2 is the CO_2 methanation. In order to perform the reaction, H_2 is required, following the stoichiometry of the Sabatier reaction (equation 2):

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad (2)$$

$$\Delta H_R^0(298\,K) = -165\,\frac{kJ}{mol}$$

In parallel to this reaction, the reverse water gas shift reaction (RWGS) occurs on the catalysts commonly employed for the reaction (2). The stoichiometry of the RWSG reaction is (equation 3):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (3)$$

$$\Delta H_R^0(298\,K) = 41\,\frac{kJ}{mol}$$

Additionally, the CO methanation reaction (linear combination of (2) and (3)) should be considered:

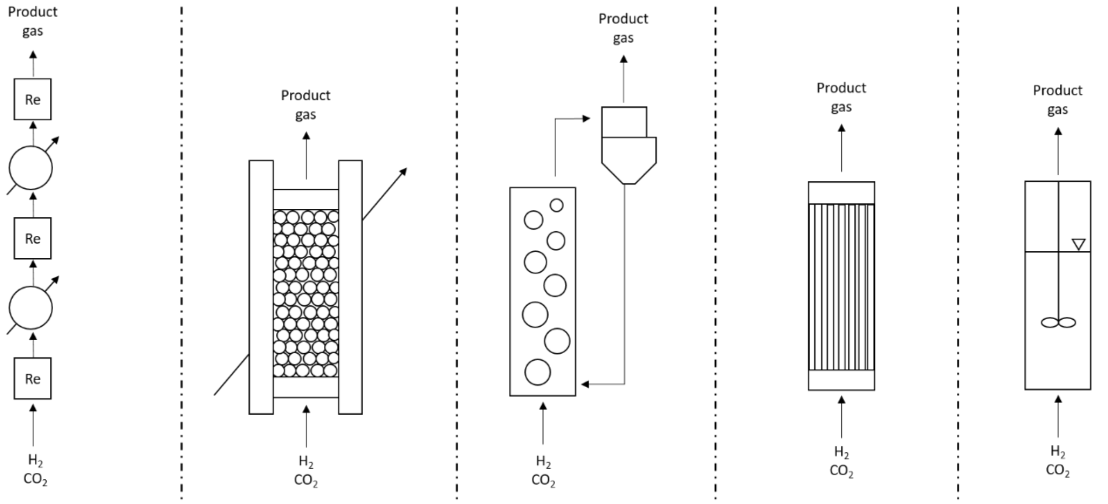
$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (4)$$

$$\Delta H_R^0(298\,K) = -206\,\frac{kJ}{mol}$$

Methanation technology has been developed since the second half of the 20th century, mainly in combination with coal gasification. The reaction was conducted in fixed bed or fluidized bed reactors [83]. Recently, new interest raised on the technology in the context of energy storage [84]. In energy storage applications, H_2 is originated from water electrolysis, operated with excess electrical energy [85]. For this reason, the cost of the produced CH_4 is strongly dependent on the electricity price and the process can be profitable only when the electricity price is low [86]. In this context, the cost of the CO_2 used in the process must be as low as possible. In this sense, the use of biogenic CO_2 shows a great potential in the Sabatier reaction. CO_2 can be obtained at low price when this is the waste of other processes, developing important advantages linked to process integration.

4.2.Reactor types

The main characteristic of the Sabatier reaction is the strong exothermicity. This leads to important challenges in the reactor design, as the heat must be efficiently removed from the system, avoiding the operation in a heat transfer limited regime [87,88] and problems related to catalyst deactivation due to sintering [89]. Several reactor types have been developed over the last few years. These include multistage adiabatic reactors, cooled fixed bed reactors, microchannel reactors and fluidized bed reactors [90]. Furthermore, the Sabatier reaction can be performed in biological reactors. The reactors are analyzed in detail in the following paragraphs and summarized in figure 5.



a) Multistage adiabatic reactor

b) Cooled fix bed reactor

c) Fluidized bed reactor

d) Microchannel reactor

e) Biological reactor

Figure 5 The available reactor types for the Sabatier reaction.

Multistage adiabatic reactor. The multistage adiabatic reactor is the oldest technology in SNG production. It has first been developed in demonstration experiments in Schwechat and Sasolburg [91]. It is now available as a semi-commercial product (TRL 8) [92]. The technology consist in a series of large vessels, in which the reaction takes place over an appropriate catalyst. The hot gases initiate the reaction, leading to runaway due to the progressively increasing heat release [93,94]. In this case, the CO_2 conversion is limited upon reaching of the thermodynamic equilibrium. The mixture of product and unreacted gas is then cooled in an intermediate cooling step, prior to a further reaction step. The number of stages, recirculation and number of feed points change according to the technology provider. In all the technologies, a pronounced hotspot is formed. Lurgi Gmbh, Vesta® (Clariant AG) and Foster Wheeler AMEC plc propose processes that limit the temperature to 550 ˚C to avoid deactivation of the catalyst [83]. Haldor Topsoe A/S and Johnson Matthey plc offer processes up to 700 ˚C, thanks to the use of catalysts more resistant to high temperature [95].

Cooled fixed bed reactor. Contrary to the adiabatic reactor, the cooled fixed bed reactor unifies reaction and cooling in one single vessel. This sensibly reduces the cost of the equipment and opens the space for reactor optimization, according to the specific cases [96–98]. An optimal profile can be obtained by adapting the cooling properties along the axial coordinate. However, the presence of a pronounced hotspot is hard to avoid. Most of the cooled reactors are composed of pipes filled with catalyst, with circulating molten salts as cooling agent [99]. Several demonstration and pilot plants for this technology exist at different scales and TRLs (generally TRL between 5-8) [100]. As an example, a multi-tubular reactor was developed by the Zentrum für Solare Wasserstofferzeugung (ZSW) in Stuttgart [101] and applied in a PtG plant in Wertle (Germany) [90,100]. This technology is now commercialized by Etogas GmbH (today part of HZI).

Fluidized bed reactor. The fluidized bed reactor technology is a state-of-the-art method to avoid the formation of an evident hotspot. This is achieved by the continuous movement of the particles, which assure spreading of the heat production over a large fraction of the reactor. Additionally, the movement of the catalyst particles usually increases the heat transfer to the cooling surfaces by turbulence effects. The catalyst particles are posed in movement by fluidisation either as gas-solid fluidised bed or as three phase reactor (bubble column) where an inert liquid phase creates a suspension of the fine catalyst particles and increases the thermal inertia [102]. The development of fluidized reactors for PtG applications started relatively recently and specific solutions were tested at the Karlsruhe Institute of Technology (Germany) [100], at the Paul Scherrer Institute (Switzerland) [2], in the EU project BioSNG [44], in the French GAYA project [90].

Structured reactors. Another strategy to improve the heat transfer in the reactor is the utilisation of fixed bed reactors filled with special materials that can improve the heat transfer by conduction (monoliths) [103,104] or by creating a strong radial convection (cross flow structures). Highly conductive metals offer a high radial conductivity between the cooled tube wall, but also a high axial conductivity, increasing the usable heat transfer area. This results in a significant reduction of the reaction hotspot and in an improved heat management. However, the use of monoliths introduces problems related to flow channelling and possible inhomogeneity in the fluid flow. This reactor type has been validated for the Sabatier reaction in the Store&Go project [105].

Biological methanation. The biological methanation reactors are significantly different than the thermo-catalytic reactors. They work at low temperature (up to 80 ˚C) and ambient pressure with methanogenic microorganism [99]. At this temperature, the reaction is not limited by thermodynamics. The main limiting factor is the mass transfer, as the reaction takes place in the fermentation broth and H_2 must reach this phase to react. For this reason, CSTR reactors are used and high stirring rate is needed [106]. The concentration of CO_2 and H_2 must be carefully controlled to avoid pH changes, which are detrimental for the microorganisms [107]. The biological methanation can take place in the digester (in-situ methanation) or in a separate reactor. When performed in a specific reactor, the process can take place also from raw materials different from biogas [108]. The reactors developed show variable methane yields [107,109,110]. The best results reported in literature show 98 % methane concentration in a trickle-bed reactor, but with low space velocity (0.4 h^{-1}) [111]. Currently, the biological methanation reactors are available as commercial plants and are offered by two providers: Microbenergy [112] and electrochaea Gmbh [113]. These commercial plants are stirred bubble columns, where the microorganisms are in an aqueous environment while CO_2 and H_2 are bubbled through the reactor. Demonstration plants are present in the BioCat project in Denmark [114], in Solothurn (CH, Store&Go project) [100] and in construction in Dietikon (CH) [115].

doi:10.20944/preprints202108.0463.v1

4.3.Comparison of the available reactors

Table 4 comparison of the main characteristics of the existing CO_2 methanation reactors

Reactor type	Adiabatic multistage	Fixed bed	Fluidized bed	Biological
Start-up temperature	>200 ˚C	250 -350 ˚C	250 -350 ˚C	50 ˚C
Reactor volume (with respect to fixed bed)	x 2	x 1	x 0.5	x 10 – 30
Specification reach upon hot start	15-30 minutes	15-30 minutes	15-30 minutes	Few minutes
TRL	8-9	6-8	6-8	8-9
Consumables needed	Catalyst	Catalyst	Catalyst	Minerals for the broth, mixer
References	[92,94,116,117]	[86,87,90,93,94,99]	[86,90,117,118]	[99,117,119,120]

The technologies analysed so far differ for several aspects, including working principle, dimensions and readiness level. A systematic comparison can be useful to understand pros and cons of the various reactor types and to understand the suitability of the systems for various applications. Table 4 reports the various characteristics of the reactors. The main difference between biological and catalytic methanation is the operating temperature. The catalytic reactors need to reach a minimal temperature (always above 200 ˚C) to activate the reaction, prior to self-sustain thanks to the heat release. This has two consequences: on one hand, the cold start of the reactor is relatively long, due to warm up to the target temperature; on the other hand, the heat produced from the reaction is at high temperature and can thus be used in further applications. The biological reactor operate at lower temperature (50-80 ˚C), showing consequently the opposite characteristics of the catalytic reactors: a short warm-up phase, but the production of heat that cannot be further utilized apart from district heating. For this reason, biological methanation cannot be used for sector coupling with systems requiring heat at high temperature. Catalytic methanation can instead be coupled with items requiring heat at temperature up to 200 ˚C, or it can be used as a preheater for example to evaporate water. This difference in temperature originate also a different performance in the warm start-up time required (time required, with the warm reactor, to produce a gas within the specifications). This time is only few minutes for biological reactors, but it sums up to more than 15 minutes for catalytic reactors. For this reason, biological methanation is suitable for applications with strongly intermittent availability of reactants, while for the catalytic methanation it is convenient to have a reservoir of H_2 and CO_2 to avoid frequent cycles of shutdown and start-up. Another important difference is in the volume required to operate the Sabatier reaction. Biological reactors require much bigger volumes, due to the difficulties in mass transfer. Among the catalytic reactors, the best performance is observed in the fluidized bed reactors, thanks to the high heat transfer present. The least performing reactor is the multistage adiabatic, due to the lack of an appropriate control of the reaction heat production. This has a direct effect on the capital cost of the equipment, with the biological reactors in the range of 1200 €/kWh$_{el}$ and the catalytic reactors at about 800 €/kWh$_{el}$ [117]. The various reactors here described differ in the degree of maturity. Biological and adiabatic reactors are available at TRL (technology readiness level) 8-9. This means they can be purchased from specific suppliers. The fixed and fluidized bed reactor do not have yet that level of maturity and are still in the demonstration phase (TRL 6-8). According to these observations, we can conclude that no ideal reactor exists for the Sabatier reaction, but the optimal technology must be carefully selected considering the specific requirements of the installation and the possibility for process integration.

4.4.Flexible use of biomass with methanation

The Sabatier reaction is a promising post-treatment reaction for biomass application. In fact, the reaction uses CO_2 as a reactant, which is largely present in biogas and in gasification gas and the main product is CH_4, which is also a product of anaerobic fermentation and gasification. It is thus evident that the coupling of the Sabatier reaction (i.e. of PtG) with fermentation and gasification can produce important synergies. On one hand, the problem of CO_2 supply in PtG can be solved by using biogenic CO_2 and, on the other hand, the need for CO_2 separation in biogas upgrading is eliminated by reacting it with H_2.

4.4.1. Hybrid biogas upgrading/SNG production

The concept of coupling of CO_2 upgrading and PtG in biogas plants is schematized in figure 6. According to the two possible processes (biogas upgrading and PtG), the product assume two different names: biomethane for the former and SNG for the latter. The coupling can be performed in two ways (figure 6):

- PtG replaces entirely upgrading when H_2 is available (A);
- PtG operates with the CO_2 deriving from the upgrading (B).

In the first case ((A) in figure 6), the two systems are strongly interconnected and the PtG section is supposed to completely convert the CO_2 present in the biogas, in order to produce a grid-compliant SNG. The main advantage of this configuration is the direct retrofitting of the biogas plant, without need for the installation of further CO_2 purification units. This is possible, for example, in biogas plants where the product is currently used in CHP to produce electricity. The retrofitted plant would then flexibly operate, switching between electricity production, when electricity price is high, and biomethane production, when the electricity price is below a certain threshold. However, this solution shows some drawbacks: the amount of H_2 required in methanation mode is fixed by the gas quality regulations (i.e. H_2 must be sufficient to convert CO_2 up to regulatory limit), thus not allowing the operation in partial load. Therefore, this system type has an intrinsic inflexibility, due to the limited possibility to switch on and off the methanation reactor. This problem can be at least partially avoided by installing an H_2 storage system (e.g. an H_2 tank) to extend the operation time.

In the second case, ((B) in figure 6), the methanation section creates a synergy with the CO_2 separation unit, alternatively converting or separating CO_2 from the biogas, according to the H_2 availability. In this case, the two units can work in parallel or in series. In the former case, biogas is fed either to upgrading or to methanation. In the latter case, the methanation unit operates with the CO_2 resulting from the separation. For the parallel configuration, no specific treatment of the biogas after gas cleaning is necessary, but the methanation reactor must be over dimensioned, due to the methane content in the biogas. For the series configuration, the advantage is a reactor that only processes a CO_2–rich stream, but the main disadvantage is that CO_2 separation section must provide a gas of the sufficient quality for the reaction. For this reason the upgrading technology must be carefully selected, as technologies such as water scrubbing or PSA may not deliver a CO_2 stream suitable for direct methanation or they would need appropriate process configurations [60]. Membranes can instead be an ideal solution for the integration of upgrading and methanation, as they can be used both for purification of biogas (from CO_2) and SNG (from CO_2 and H_2) [121]. When CO_2 is directly obtained and purified from the gas upgrading unit, it is possible to install a CO_2 storage unit, which can increase the flexibility of the system.

Biogas upgrading is currently regarded as an important option for the implementation of PtG. Several demonstration plants were installed in the world and research is still highly active in this field [100]. The main advantage in the use of biogas as feedstock in PtG is the compatible scale of the two systems, as the quantity of CO_2 available is limited, thus not requiring a large amount of H_2 (from large power plants) for operation.

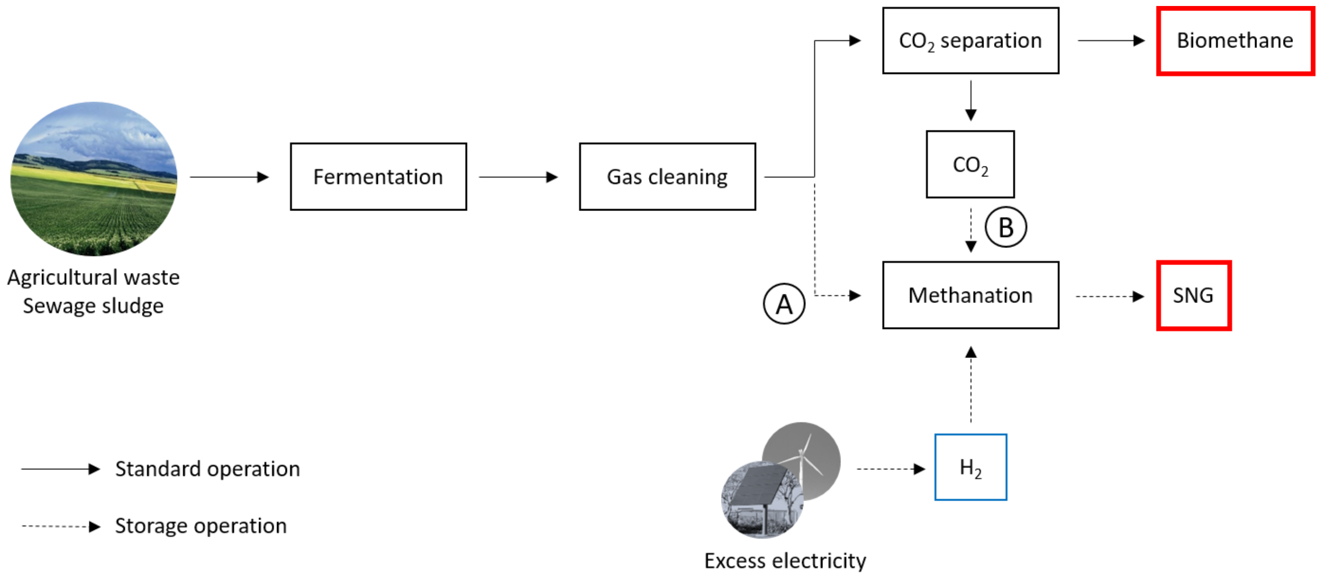


Figure 6 Process flow diagram of the flexible use of biomass

4.4.2. Hybrid biomethane/SNG production from gasification

The integration of gasification and energy storage is an important opportunity for the development of a flexible process for the use of biomass. As observed in figure 2, various gasifiers can be used for the production of a CO_2 neutral SNG. DFB, SER and BFB produce gas mixtures containing significant amount of CH_4, as well as CO, CO_2 and H_2. In the post-treatment of this gas, it is possible to focus on the production of biomethane, optimizing the energy yield of the biomass [22] (following the processes described in section 2.2). In this case, the process can be adapted to the flexible use of this biogenic gas, involving the utilisation of H_2 produced from renewable resources (e.g. electrolysis) to increase the CO and CO_2 conversion, as shown in figure 7. This can be performed in the specific methanation unit already installed in the process. When additional external H_2 is available, this is added to the biogas in the methanation reactor, producing further SNG. In this sense, the gasification plant operates both as a biogas production unit and as an energy storage facility. Compared to the similar concept developed for anaerobic fermentation, the flexible use of gasification shows lower process complexity, as the methanation unit is used in both conditions (biogas and storage) and the CO_2 separation remains in operation to remove the remaining CO_2 eventually present. In this way, the process can be operated also in the presence of low amounts of H_2. In synthesis, the transformation of a wood gasification plant into a flexible biogas-PtG requires limited additional investment, as the main units are already present in the standard configuration. However, the system here presented shows a higher level of complexity compared to the flexible anaerobic digestion, due to the intrinsic complication of the gasification system. The large amount of units necessary for the cleaning and reforming of the gasification products require a careful heat and process integration, which can be performed only for large-scale plants. For this reason, only plants above 100 MW_{prod} can result profitable [122]. This is an important limitation for the development of this plant type, because large amounts of biomass may be not available in an economically reasonable distance from the planned plants, thus preventing the geographically uniform development of the technology [54]. Plants for this type of flexible use of woody biomass exist at demonstration scale (TRL 6-7). Examples are the Güssing SNG production in Austria [23] and the GoBiGas project in Sweden [123]. The cost estimated for the produced SNG from this type of plant is about 60 €/MWh_{SNG}, with the feedstock accounting for ca. 40 % of the production cost [122]. It is therefore evident that the biomass availability is the key for the further development of the technology.

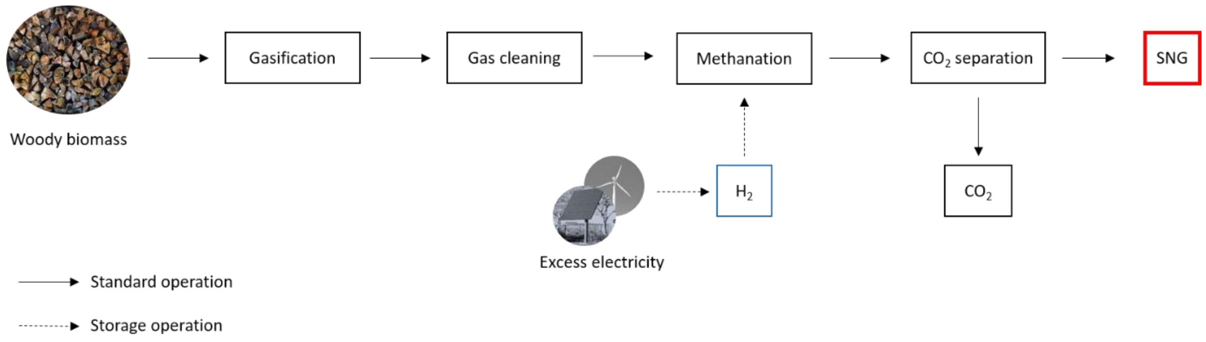


Figure 7 Flexible use of wood for biomethane production and energy storage

5. Processes for the production of liquid fuels from biogenic CO_2

Apart from SNG production, the biomass valorisation can be coupled with other PtX processes. Particular interest is linked to the production of chemicals liquid at ambient conditions, as these can be stored over long time in the existing facilities for liquid fuels. Furthermore, they can be reconverted in electricity at any time using the standard power plants [124]. Several target molecules can be the object of PtX [125] and biomass valorisation strategies [22]. However, the most studied molecules to substitute liquid fuels are methanol and hydrocarbons.

5.1.Methanol

Methanol (MeOH) is currently one of the most produced commodities worldwide and it is widely used in the chemical industry. The interest for MeOH as a fuel is originated by its high octane number, which makes this molecule an optimal additive or substitute for gasoline [126,127]. MeOH can also be used as a feedstock for the production of DME, which is an optimal diesel substitute [22].

The reaction to produce methanol from CO_2 and H_2 follows the stoichiometry of equation 5:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{5}$$

$$\Delta H_R^0(298\,K) = -49.5\,\frac{kJ}{mol}$$

The reaction is shifted towards the reactants at high temperature, so that the conversion per pass, at the temperature of activation of the standard $Cu/ZnO/Al_2O_3$ catalysts (250-300 ˚C), is low [128]. For this reason, the commercial processes use high pressure and large recycle streams [129]. The CO_2 to methanol reaction has been widely investigated, to find an appropriate process configuration to efficiently produce methanol with comparable costs to the commercial process. However, the cost of CO_2 and renewable H_2 and the need for compression to high pressure affect significantly the production costs [130]. For this reason, the current technologies can be employed in the PtMeOH process only by implementing an effective process integration at large scale (> 50 kt_{MeOH}/y) [131,132]. The PtMeOH technology has therefore been implemented only in few locations, where the cost of electricity can be particular low. This is the case, for example, of the George Olah plant by Carbon Recycling International in Iceland. Here, a plant producing 5 Mt_{MeOH}/y can be operated thanks to the access to cheap electricity and CO_2 (from geothermal sources). Mitsui chemicals built a plant in Japan to produce around 100 t_{MeOH}/y, using CO_2 from factories [133].

An interesting example of flexible methanol production comes from the Carb2Chem project that is currently focusing at the production of methanol from steel mill gases [134]. In this plant, the hot gases are either used for energy production (when electricity price is high) or for methanol production (when electricity price is low and the electrolyser is operated). In this case, a standard methanol reactor can be operated thanks to the large gas flow and the high temperature of the gas at the source.

Considered the examples above, the PtMeOH technology is thus currently at TRL 6-7 [133].

For what concerns the methanol production from biomass resources, we can derive some suggestion according to the available demonstration. As the currently available technology can be profitable only at large scale, this can be employed only with large supply of biomass, as in the case of wood gasification. It is then possible to imagine the coupling of wood gasification and methanol production, if cheap electricity is available on site [132]. As in the case of methane production, the main drawback of this solution is the need of large amounts of biomass, which requires an important effort (and cost) in term of logistics. For this reason, the installation of this type of plant is possible only in specific geographical context, where the required biomass (equivalent to >1 t_{MeOH}/d) can be collected in a reasonable radius from the plant. Over the last decades, several plants have been developed to this purpose and using various feedstock types [22].

The methanol production at lower scale is not feasible with the current technology due to the incidence of compression costs [133]. This rules out the possibility of using directly the CO_2

originated from small-scale biogas plant. The use of this type of biogenic CO_2 can be hypothesized only if this latter can be collected in a centralized unit or if a new small-scale reactor technology is developed. For the former case, important infrastructural investment are necessary, which should collect the CO_2 from biogas plants and direct it to a centralized plant for the production of methanol where the ideal conditions are met (i.e. large availability of cheap electricity) above the critical scale. Unfortunately, the implementation of such an infrastructure is currently far from reality [135]. In the latter case, specific catalysts for the methanol synthesis at lower temperature and pressure are needed. Research is largely active in this field, but a commercial catalyst for this scope is not yet available [136,137].

5.2.Hydrocarbons

Higher hydrocarbon can be synthesized from syngas in the Fischer-Tropsch (FT) synthesis. FT has been developed starting from coal gasification or from natural gas [138] but also demonstration plants from biomass exist [139–141]. The FT synthesis yields a series of products, containing a different number of carbon atoms, following the stoichiometry of reaction (6) and (7) from CO and CO_2, respectively:

$$nCO + 2n\,H_2 \leftrightarrow C_nH_{2n+2} + nH_2O \tag{6}$$

$$nCO_2 + (3n+1)\,H_2 \leftrightarrow C_nH_{2n+2} + 2nH_2O \tag{7}$$

As mentioned in section 2.2, the gasification process can be tailored for this synthesis, obtaining an optimal $CO/CO_2/H_2$ ratio. However, general $CO:H_2$ ratios obtained from biomass can be lower than the required 1:2, down to 0.7:1 [142]. This can be in part solved by use of Fe-based catalysts, which are active in the WGS reaction [143]. Alternatively, the $CO:H_2$ ratio can be adjusted by coupling the biomass to liquid (BtL) process with Power-to-Liquids (PtL). In this sense, renewable H_2 can be used to improve the stoichiometric ratio of the gasification products, taking advantage of the CO already present in the gas stream. In fact, the reaction CO_2 to liquid fuels is challenging and the various catalytic technologies are being validated only at lab scale (TRL 1-4) [144–146]. The PtL technology would thus mainly base on the conversion of CO_2 into CO in a dedicated unit prior to the FT synthesis. This has the disadvantage of requiring a reactive step at high temperature, needing for external heat. Without prior conversion of CO_2, the standard Co catalyst is not effective in the FT synthesis and the available Fe-based catalysts are unselective and show low conversion [147]. These limitations hinder the development of the PtL technology, but its use in combination with BtL may generate important advantages in terms of process management and reactor design. In this way, a system as depicted in figure 8 can be operated integrating energy storage and hydrocarbon production.

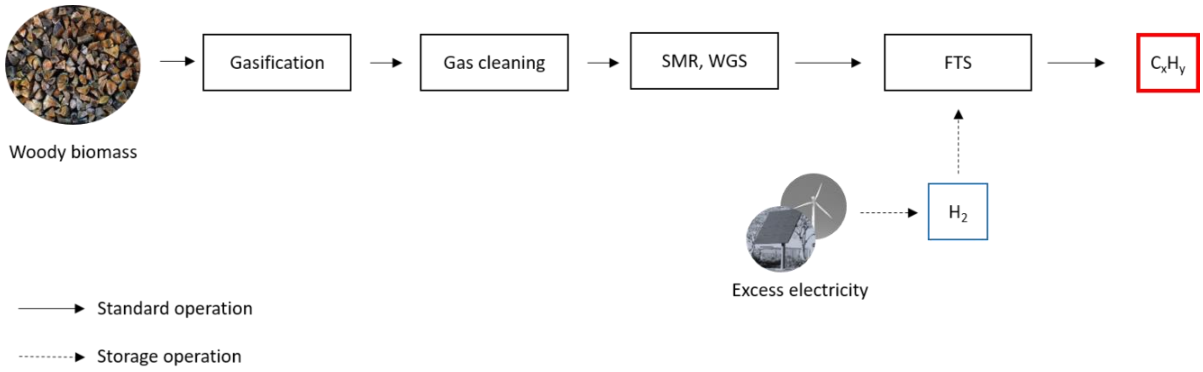


Figure 8 Process flow diagram of the BtL/PtG hybrid process. (SMR=Steam Methane Reforming, WGS=Water Gas Shift, FTS= Fischer-Tropsch Synthesis)

6. Conclusions

In this review, we analysed the available technologies for the flexible employment of biomass as a resource to build the future energy system enabling the alternatives: storage of renewable energy or the implementation of negative emissions. We studied the currently employed strategies to produce biogas from agricultural/urban waste, sewage sludge and woody biomass and the available technologies for biogas cleaning and upgrading. Furthermore, we underlined how biomass utilisation and energy storage can be coupled to enhance the flexibility of the energy systems and the sustainable production of carbon neutral fuels.

Biomass can operate as a reliable source of carbon for the energy system, becoming an ideal substitute of the currently used fossil fuels. The technologies for biogenic gas production from agricultural/urban waste already reached full commercial maturity; the technologies based on wood gasification have been successfully demonstrated. They constitute the platform for the production of a carbon neutral substitute of the natural gas. Furthermore, as CO_2 is produced alongside with CH_4, the former can be separated and used in further processes. When CO_2 is captured after the separation and permanently stored (CCS), the result is the realization of negative CO_2 emissions. We observed that the amount of CO_2 that can be captured in this way is up to 40-50 % of the initial biomass carbon content for anaerobic digestion and up to 50 % for the wood gasification. This biogenic-originated CO_2 can be used as a cheap feedstock in the production of synthetic fuels from renewable H_2 when renewable electricity is available that otherwise cannot be used. In this way, a reliable and continuous source of carbon is provided to the energy system, providing an efficient and flexible coupling of the electric grid with the gas and fuels networks. We observed that several methods for the separation of CO_2 from CH_4 are available. However, not all of them are suitable for the coupling with synthetic fuel production. In this sense, only amine scrubbers and membranes can effectively be employed to this scope. The produced CO_2 can be directly used in reactions with H_2 or stored (preferably in liquefied form) over long periods prior to utilization or until transport to sequestration sites for negative CO_2 emissions. The technologies for the flexible utilisation of biomass towards the production of biomethane/SNG (amine scrubbers, membranes, catalytic and biological reactors) are available at commercial or semi-commercial scale (TRL 6-9) and can be employed at various scales, thanks to their simple design. The technologies for the production of liquid fuels (e.g. methanol and hydrocarbons) are less mature (TRL $\leq$6) and more subject to efficiency of scale, making the application at small-scale economically challenging.

doi:10.20944/preprints202108.0463.v1

The biogas chain is thus most suitable for the production of renewable natural gas in locations with limited supply of biomass resources.

The energetic valorisation of woody biomass requires the processing at high temperature, hence creating the need for larger scale compared to the biogas applications. Furthermore, because of thermodynamics at high temperature, the product gas is a complex mixture that must be treated to obtain the desired products. For these chemical reactions, larger units of at least MW scale are necessary, increasing the need for process integration. Large amounts of biomass are thus required for the operation of these plants, creating problems of feedstock supply in certain regions. For this reason, efficient wood gasification plants can be installed in specific geographical location, where the access to sufficient amount of biomass is granted in short distance. These factors limited the development of the biomass gasification technology, which is currently available only at pre-commercial scale. However, the biomass gasification process has a large potential in the energy systems of the future, as it can provide a complementary platform to the biogas value chain. In fact, the larger scale of the facilities allows the process integration with the routes producing methanol and hydrocarbons. In particular, the combination of BtL processes (producing hydrocarbons and alcohols during the entire year) and PtL (storing renewable energy in the form of liquid fuels at peak availability times) can open the way for significant efficiency improvements and for an important increase in the flexibility of the energy system.

In conclusion, biomass resources can provide an important platform for the development of the energy system of the future, as they can constantly supply carbon neutral fuels and are a continuous source of CO_2 for the implementation of PtX strategies for energy storage, becoming the key bridge among electrical grid, natural gas network and liquid fuel distribution. Additionally, the available technologies can be easily retrofitted with carbon capture operations, enabling negative CO_2 emissions when CO_2 cannot be valorised by reaction with renewable H_2. Most of the required technologies are already available at commercial or semi-commercial scale and require of implementation at large scale to become completely profitable, creating a complete and efficient energy supply chain based on biomass.

Acknowledgement

This work was conducted within the framework of the IEA Bioenergy task 44: Flexible bioenergy

Nomenclature

ASU = Air Separation Unit

BFB = Bubbling Fluidized Bed Reactor

BtL = Biomass to Liquid

CA = Cellulose Acetate Membrane

CCS = Carbon Capture and Storage

CCU = Carbon Capture and Utilisation

CHP = Combined Heat and Power Production

CSTR = Continuously Stirred Tank Reactor

DAC = Direct Air Capture

DFB = Dual Fluidised Bed Reactor

EF = Entrained Flow Reactor

FT = Fischer-Tropsch Synthesis

ICE = Internal Combustion Engine

IGCC = Integrated Gasification Combined Cycle

MEA = Mono Ethanol Amine

MeOH = Methanol

MMMs = Mixed Matrix Membranes

MOF = Metal Organic Frameworks

MSR = Methane Steam Reforming

PC = PolyCarbonate Membranes

PI = PolyImide Membranes

PSA = Pressure Swing Adsorption

PsF = Polysulphone Membranes

PtG = Power to Gas

PtL= Power to Liquids

PtMeOH = Power to Methanol

PtX = Power to X

RT = Room Temperature

RWGS = Reverse Water Gas Shift Reaction

SAPO = Silico-Alumino-Phosphate

SER = Sorption Enhanced Reforming

SOFC = Solid Oxide Fuel Cells

SNG = Synthetic Natural Gas

WGS = Water Gas Shift Reaction

ΔH^R = reaction enthalpy (kJ/mol)

References

[1] Marxer D, Furler P, Scheffe J, Geerlings H, Falter C, Batteiger V, et al. Demonstration of the entire production chain to renewable kerosene via solar thermochemical splitting of H2O and CO2. Energy and Fuels 2015;29:3241–50. https://doi.org/10.1021/acs.energyfuels.5b00351.

[2] Witte J, Calbry-Muzyka A, Wieseler T, Hottinger P, Biollaz SMA, Schildhauer TJ. Demonstrating direct methanation of real biogas in a fluidised bed reactor. Appl Energy

2019;240:359–71. https://doi.org/10.1016/j.apenergy.2019.01.230.

[3] Torp TA, Gale J. Demonstrating storage of CO2 in geological reservoirs: The Sleipner and SACS projects. Energy 2004;29:1361–9. https://doi.org/10.1016/j.energy.2004.03.104.

[4] Antonini C, Treyer K, Moioli E, Bauer C, Schildhauer T, Mazzotti M. Hydrogen from wood gasification with CCS - a techno-environmental analysis of production and use as transport fuel. Sustain Energy Fuels 2021. https://doi.org/10.1039/d0se01637c.

[5] Schildhauer TJ. Biosynthetic Natural Gas (Bio-SNG). Energy from Org. Mater., 2019, p. 1065–80. https://doi.org/10.1007/978-1-4939-7813-7_996.

[6] Thees O, Burg V, Erni M, Bowman G, Lemm R. Biomassepotenziale der Schweiz für die energetische Nutzung, Ergebnisse des Schweizerischen Energiekompetenzzentrums SCCER BIOSWEET. WSL Bericht 2017;57:299.

[7] Yadvika, Santosh, Sreekrishnan TR, Kohli S, Rana V. Enhancement of biogas production from solid substrates using different techniques - A review. Bioresour Technol 2004;95:1–10. https://doi.org/10.1016/j.biortech.2004.02.010.

[8] Koniuszewska I, Korzeniewska E, Harnisz M, Czatzkowska M. Intensification of biogas production using various technologies: A review. Int J Energy Res 2020;44:6240–58. https://doi.org/10.1002/er.5338.

[9] De Bok FAM, Van Leerdam RC, Lomans BP, Smidt H, Lens PNL, Janssen AJH, et al. Degradation of methanethiol by methylotrophic methanogenic archaea in a lab-scale upflow anaerobic sludge blanket reactor. Appl Environ Microbiol 2006;72:7540–7. https://doi.org/10.1128/AEM.01133-06.

[10] Vergara-Fernández A, Vargas G, Alarcón N, Velasco A. Evaluation of marine algae as a source of biogas in a two-stage anaerobic reactor system. Biomass and Bioenergy 2008;32:338–44. https://doi.org/10.1016/j.biombioe.2007.10.005.

[11] Abbassi-Guendouz A, Trably E, Hamelin J, Dumas C, Steyer JP, Delgenès JP, et al. Microbial community signature of high-solid content methanogenic ecosystems. Bioresour Technol 2013;133:256–62. https://doi.org/10.1016/j.biortech.2013.01.121.

[12] European Biogas Association. European Biomethane Map 2018:1.

[13] Merlin Christy P, Gopinath LR, Divya D. A review on anaerobic decomposition and enhancement of biogas production through enzymes and microorganisms. Renew Sustain Energy Rev 2014;34:167–73. https://doi.org/10.1016/j.rser.2014.03.010.

[14] Cavinato C, Fatone F, Bolzonella D, Pavan P. Thermophilic anaerobic co-digestion of cattle manure with agro-wastes and energy crops: Comparison of pilot and full scale experiences. Bioresour Technol 2010;101:545–50. https://doi.org/10.1016/j.biortech.2009.08.043.

[15] Awe OW, Zhao Y, Nzihou A, Minh DP, Lyczko N. A Review of Biogas Utilisation, Purification and Upgrading Technologies. Waste and Biomass Valorization 2017;8:267–83. https://doi.org/10.1007/s12649-016-9826-4.

[16] Calbry-Muzyka AS, Gantenbein A, Schneebeli J, Frei A, Knorpp AJ, Schildhauer TJ, et al. Deep removal of sulfur and trace organic compounds from biogas to protect a catalytic methanation reactor. Chem Eng J 2019;360:577–90. https://doi.org/10.1016/j.cej.2018.12.012.

[17] Dewil R, Appels L, Baeyens J. Energy use of biogas hampered by the presence of siloxanes. Energy Convers Manag 2006;47:1711–22. https://doi.org/10.1016/j.enconman.2005.10.016.

[18] Persson M, Jonsson O, Wellinger A. Biogas Upgrading To Vehicle Fuel Standards and Grid. IEA Bioenergy 2007:1–32.

[19] Allegue LB, Hinge J. Biogas upgrading Evaluation of methods for H 2 S removal. Danish Technol Inst 2014:31. https://doi.org/10.1074/mcp.M110.002766.

[20] Hosseini SE, Wahid MA. Development of biogas combustion in combined heat and power generation. Renew Sustain Energy Rev 2014;40:868–75. https://doi.org/10.1016/j.rser.2014.07.204.

[21] Higman C, van der Burgt M. Gasification. Elsevier B.V.; 2008. https://doi.org/10.1016/B978-0-7506-8528-3.X0001-6.

[22] Sikarwar VS, Zhao M, Fennell PS, Shah N, Anthony EJ. Progress in biofuel production from gasification. Prog Energy Combust Sci 2017;61:189–248. https://doi.org/10.1016/j.pecs.2017.04.001.

[23] Heyne S, Seemann M, Schildhauer TJ. Synthetic Natural Gas from Coal, Dry Biomass, and POWER-TO-GAS Applications n.d.

[24] Sansaniwal SK, Pal K, Rosen MA, Tyagi SK. Recent advances in the development of biomass gasification technology: A comprehensive review. Renew Sustain Energy Rev 2017;72:363–84. https://doi.org/10.1016/j.rser.2017.01.038.

[25] Heyne S, Thunman H, Harvey S. Exergy-based comparison of indirect and direct biomass gasification technologies within the framework of bio-SNG production. Biomass Convers Biorefinery 2013;3:337–52. https://doi.org/10.1007/s13399-013-0079-1.

[26] Meerman JC, Ramírez A, Turkenburg WC, Faaij APC. Performance of simulated flexible integrated gasification polygeneration facilities, Part B: Economic evaluation. Renew Sustain Energy Rev 2012;16:6083–102. https://doi.org/10.1016/j.rser.2012.06.030.

[27] Hansson J, Leveau A. Biomass Gasifier Database for Computer Simulation Purposes 2011:1–42.

[28] Binder M, Kraussler M, Kuba M, Luisser M. Hydrogen from biomass. 2018. https://doi.org/10.1016/b978-008043947-1/50003-x.

[29] Schmid, Johannes Christian MÜLLER S, KOLBITSCH M, TESCH W, HOFBAUER H. G - VOLUTION II Zweibettwirbelschicht Biomasse - Dampfvergaser Inhaltsverzeichnis. 2015.

[30] Harris DJ, Roberts DG. Coal gasification and conversion. Coal Handb Towar Clean Prod 2013;2:427–54. https://doi.org/10.1533/9781782421177.3.427.

[31] BIOTFUEL : DEVELOPING SECOND-GENERATION BIOFUELS n.d. https://www.total.com/energy-expertise/projects/bioenergies/biotfuel-converting-plant-wastes-into-fuel.

[32] Willkommen bei bioliq® © n.d. www.bioliq.de.

[33] Rhyner U. Gas Cleaning. Synth. Nat. Gas from Coal, Dry Biomass, POWER-TO-GAS Appl., 2016, p. 41–76.

[34] Krause D, Herdel P, Ströhle J, Epple B. HTW^{TM}-gasification of high volatile bituminous coal in a 500 kWth pilot plant. Fuel 2019;250:306–14. https://doi.org/10.1016/j.fuel.2019.04.014.

[35] Franken G, Adlhoch W, Koch W. Herstellung von Synthesegas aus Braunkohle. Chemie Ing Tech 1980;52:324–7. https://doi.org/10.1002/cite.330520407.

[36] High Temperature Winkler (HTW) Gasifier | netl.doe.gov n.d. https://www.netl.doe.gov/research/Coal/energy-systems/gasification/gasifipedia/winkler.

[37] Värmlandsmetanol. World ' s first Commercial Scale Biomethanol Plant in Hagfors SWEDEN Biomass as received District heat export Methanol energy 2012:11.

[38] Hrbek J. Status report on thermal biomass gasification in countries participating in IEA Bioenergy Task 33 2016:163.

[39] Patel J, Salo K, Horvath A J. ANDRITZ Carbona Biomass Gasification Process for Power and Bio Fuels. Eur. Biomass Conf. Exhib. ETA-Florence Renew. Energies,

Copenhagen, denmark; 2013., 2013.

[40] Gas Technology Institute. Low-Carbon Renewable Natural Gas (RNG) from Wood Wastes 2019:86.

[41] Corella J, Toledo JM, Molina G. A review on dual fluidized-bed biomass gasifiers. Ind Eng Chem Res 2007;46:6831–9. https://doi.org/10.1021/ie0705507.

[42] Benedikt F, Schmid JC, Fuchs J, Mauerhofer AM, Müller S, Hofbauer H. Fuel flexible gasification with an advanced 100 kW dual fluidized bed steam gasification pilot plant. Energy 2018;164:329–43. https://doi.org/10.1016/j.energy.2018.08.146.

[43] Kuba M, Havlik F, Kirnbauer F, Hofbauer H. Influence of bed material coatings on the water-gas-shift reaction and steam reforming of toluene as tar model compound of biomass gasification. Biomass and Bioenergy 2016;89:40–9. https://doi.org/10.1016/j.biombioe.2015.11.029.

[44] Rehling B, Hofbauer H, Rauch R, Aichernig C. BioSNG-process simulation and comparison with first results from a 1-MW demonstration plant. Biomass Convers Biorefinery 2011;1:111–9. https://doi.org/10.1007/s13399-011-0013-3.

[45] Larsson A, Gunnarsson I, Tengberg F. The GoBiGas Project 2018:52.

[46] Meijden CM Van Der, Veringa HJ, Drift A Van Der, Vreugdenhil BJ. The 800 kWth allothermal biomass gasifier MILENA. 16th Eur Biomass Conf 2008:2–6.

[47] Schmid JC. ERBAII - Optimierung von „Sorption Enhanced Reforming“ zur Verbesserung der CO2-Bilanz in der Roheisenerzeugung mittels Biomasse. 2017.

[48] Pfeifer C, Puchner B, Hofbauer H. Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO2. Chem Eng Sci 2009;64:5073–83. https://doi.org/10.1016/j.ces.2009.08.014.

[49] Koppatz S, Pfeifer C, Rauch R, Hofbauer H, Marquard-Moellenstedt T, Specht M. H2 rich product gas by steam gasification of biomass with in situ CO2 absorption in a dual

fluidized bed system of 8 MW fuel input. Fuel Process Technol 2009;90:914–21. https://doi.org/10.1016/j.fuproc.2009.03.016.

[50] Rhyner U, Edinger P, Schildhauer TJ, Biollaz SMA. Applied kinetics for modeling of reactive hot gas filters. Appl Energy 2014;113:766–80. https://doi.org/10.1016/j.apenergy.2013.07.063.

[51] Liu K, Song C, Subramani V. Hydrogen and Syngas Production and Purification Technologies. WILEY-VCH Verlag; 2010. https://doi.org/10.1016/s1351-4180(10)70287-7.

[52] Fail S, Diaz N, Benedikt F, Kraussler M, Hinteregger J, Bosch K, et al. Wood gas processing to generate pure hydrogen suitable for PEM fuel cells. ACS Sustain Chem Eng 2014;2:2690–8. https://doi.org/10.1021/sc500436m.

[53] Bowen D, Lau F, Zabransky RR, Slimane R, Doong S. Techno-economic analysis of hydrogen production by gasification of biomass. Hydrog Fuel Cells, Infrastruct Technol 2003:4.

[54] Henrich E. The status of the FZK concept of biomass gasification. Warsaw Summer Sch., 2007, p. 29–31.

[55] Neves RC, Klein BC, da Silva RJ, Rezende MCAF, Funke A, Olivarez-Gómez E, et al. A vision on biomass-to-liquids (BTL) thermochemical routes in integrated sugarcane biorefineries for biojet fuel production. Renew Sustain Energy Rev 2020;119. https://doi.org/10.1016/j.rser.2019.109607.

[56] He L, Yang J, Chen D. Hydrogen from Biomass: Advances in Thermochemical Processes. Renew Hydrog Technol Prod Purification, Storage, Appl Saf 2013:111–33. https://doi.org/10.1016/B978-0-444-56352-1.00006-4.

[57] Mueller-Langer F, Tzimas E, Kaltschmitt M, Peteves S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium

term. Int J Hydrogen Energy 2007;32:3797–810. https://doi.org/10.1016/j.ijhydene.2007.05.027.

[58] Ryckebosch E, Drouillon M, Vervaeren H. Techniques for transformation of biogas to biomethane. Biomass and Bioenergy 2011;35:1633–45. https://doi.org/10.1016/j.biombioe.2011.02.033.

[59] Kapoor R, Ghosh P, Kumar M, Vijay VK. Evaluation of biogas upgrading technologies and future perspectives : a review. Env Sci Pollut Res 2019. https://doi.org/https://doi.org/10.1007/s11356-019-04767-1.

[60] Collet P, Flottes E, Favre A, Raynal L, Pierre H, Capela S, et al. Techno-economic and Life Cycle Assessment of methane production via biogas upgrading and power to gas technology. Appl Energy 2017;192:282–95. https://doi.org/10.1016/j.apenergy.2016.08.181.

[61] Angelidaki I, Treu L, Tsapekos P, Luo G, Campanaro S, Wenzel H, et al. Biogas upgrading and utilization: Current status and perspectives. Biotechnol Adv 2018;36:452–66. https://doi.org/10.1016/j.biotechadv.2018.01.011.

[62] Bauer F, Hulteberg C, Persson T, Tamm D. Biogas upgrading – Review of commercial technologies (Biogasuppgradering – Granskning av kommersiella tekniker); Catalyzing energy gas development for sustainable solutions 2013:1–81.

[63] Ullah Khan I, Hafiz Dzarfan Othman M, Hashim H, Matsuura T, Ismail AF, Rezaei-DashtArzhandi M, et al. Biogas as a renewable energy fuel – A review of biogas upgrading, utilisation and storage. Energy Convers Manag 2017;150:277–94. https://doi.org/10.1016/j.enconman.2017.08.035.

[64] Grande CA. Advances in Pressure Swing Adsorption for Gas Separation. ISRN Chem Eng 2012;2012:1–13. https://doi.org/10.5402/2012/982934.

[65] Cucchiella F, D’Adamo I. Technical and economic analysis of biomethane: A focus on

the role of subsidies. Energy Convers Manag 2016;119:338–51. https://doi.org/10.1016/j.enconman.2016.04.058.

[66] Muñoz R, Meier L, Diaz I, Jeison D. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. Rev Environ Sci Biotechnol 2015;14:727–59. https://doi.org/10.1007/s11157-015-9379-1.

[67] Chen XY, Vinh-Thang H, Ramirez AA, Rodrigue D, Kaliaguine S. Membrane gas separation technologies for biogas upgrading. RSC Adv 2015;5:24399–448. https://doi.org/10.1039/c5ra00666j.

[68] Scholz M, Melin T, Wessling M. Transforming biogas into biomethane using membrane technology. Renew Sustain Energy Rev 2013;17:199–212. https://doi.org/10.1016/j.rser.2012.08.009.

[69] Thema M, Weidlich T, Hörl M, Bellack A, Mörs F, Hackl F, et al. Biological CO 2 -Methanation : An Approach. Energies 2019;12:1–32.

[70] Petronela C, Wukovits W, Mamaliga I, Friedl A. Analysis and modelling of the solubility of biogas components in water for physical absorption processes ANALYSIS AND MODELLING OF THE SOLUBILITY OF BIOGAS COMPONENTS IN WATER FOR PHYSICAL ABSORPTION PROCESSES 2013. https://doi.org/10.30638/eemj.2013.017.

[71] Läntelä J, Rasi S, Lehtinen J, Rintala J. Landfill gas upgrading with pilot-scale water scrubber: Performance assessment with absorption water recycling. Appl Energy 2012;92:307–14. https://doi.org/10.1016/j.apenergy.2011.10.011.

[72] Nock WJ, Walker M, Kapoor R, Heaven S. Modeling the water scrubbing process and energy requirements for CO 2 capture to upgrade biogas to biomethane. Ind Eng Chem Res 2014;53:12783–92. https://doi.org/10.1021/ie501280p.

[73] Wilken D, Strippel F, Hofmann F, Maciejczyk M, Klinkmüller L, Wagner L, et al.

Biogas to Biomethane. Unido 2017:9.

[74] Andriani D, Wresta A, Atmaja TD, Saepudin A. A review on optimization production and upgrading biogas through CO 2 removal using various techniques. Appl Biochem Biotechnol 2014;172:1909–28. https://doi.org/10.1007/s12010-013-0652-x.

[75] Mani F, Peruzzini M, Stoppioni P. CO2 absorption by aqueous NH3 solutions: Speciation of ammonium carbamate, bicarbonate and carbonate by a 13C NMR study. Green Chem 2006;8:995–1000. https://doi.org/10.1039/b602051h.

[76] Kadam R, Panwar NL. Recent advancement in biogas enrichment and its applications. Renew Sustain Energy Rev 2017;73:892–903. https://doi.org/10.1016/j.rser.2017.01.167.

[77] Tagliabue M, Farrusseng D, Valencia S, Aguado S, Ravon U, Rizzo C, et al. Natural gas treating by selective adsorption: Material science and chemical engineering interplay. Chem Eng J 2009;155:553–66. https://doi.org/10.1016/j.cej.2009.09.010.

[78] Pertl A, Mostbauer P, Obersteiner G. Climate balance of biogas upgrading systems. Waste Manag 2010;30:92–9. https://doi.org/10.1016/j.wasman.2009.08.011.

[79] Basu S, Khan AL, Cano-Odena A, Liu C, Vankelecom IFJ. Membrane-based technologies for biogas separations. Chem Soc Rev 2010;39:750–68. https://doi.org/10.1039/b817050a.

[80] Chmielewski AG, Urbaniak A, Wawryniuk K. Membrane enrichment of biogas from two-stage pilot plant using agricultural waste as a substrate. Biomass and Bioenergy 2013;58:219–28. https://doi.org/10.1016/j.biombioe.2013.08.010.

[81] Abderezzak B, Khelidj B, Kellaci A, Abbes MT. The Smart Use of Biogas: Decision Support Tool. AASRI Procedia 2012;2:156–62. https://doi.org/10.1016/j.aasri.2012.09.028.

[82] Balussou D, Heffels T, McKenna R, Möst D, Fichtner W. An evaluation of optimal

biogas plant configurations in Germany. Waste and Biomass Valorization 2014;5:743–58. https://doi.org/10.1007/s12649-013-9284-1.

[83] Kopyscinski J, Schildhauer TJ, Biollaz SMA. Production of synthetic natural gas (SNG) from coal and dry biomass - A technology review from 1950 to 2009. Fuel 2010;89:1763–83. https://doi.org/10.1016/j.fuel.2010.01.027.

[84] Aziz MAA, Jalil AA, Triwahyono S, Ahmad A. CO 2 methanation over heterogeneous catalysts: recent progress and future prospects. Green Chem 2015;17:2647–63. https://doi.org/10.1039/C5GC00119F.

[85] Schiebahn S, Grube T, Robinius M, Tietze V, Kumar B, Stolten D. Power to gas: Technological overview, systems analysis and economic assessment for a case study in Germany. Int J Hydrogen Energy 2015;40:4285–94. https://doi.org/10.1016/j.ijhydene.2015.01.123.

[86] Witte J, Kunz A, Biollaz SMA, Schildhauer TJ. Direct catalytic methanation of biogas – Part II: Techno-economic process assessment and feasibility reflections. Energy Convers Manag 2018;178:26–43. https://doi.org/10.1016/j.enconman.2018.09.079.

[87] Moioli E, Züttel A. A model-based comparison of Ru and Ni catalysts for the Sabatier reaction. Sustain Energy Fuels 2020;4:1396–408. https://doi.org/10.1039/c9se00787c.

[88] Moioli E, Gallandat N, Züttel A. Model based determination of the optimal reactor concept for Sabatier reaction in small-scale applications over Ru/Al2O3. Chem Eng J 2019;375:121954. https://doi.org/10.1016/j.cej.2019.121954.

[89] Gao J, Liu Q, Gu F, Liu B, Zhong Z, Su F. Recent advances in methanation catalysts for the production of synthetic natural gas. RSC Adv 2015;5:22759–76. https://doi.org/10.1039/C4RA16114A.

[90] Rönsch S, Schneider J, Matthischke S, Schlüter M, Götz M, Lefebvre J, et al. Review on methanation - From fundamentals to current projects. Fuel 2016;166:276–96.

https://doi.org/10.1016/j.fuel.2015.10.111.

[91] Moeller FW, Roberts H, Britz B. Methanation of Coal Gas for Sng. Hydrocarb Process 1974;53:69–74.

[92] Held J. The GoBiGas project. In: Schildhauer TJ, Biollaz SMA, editors. Synth. Nat. Gas from Coal, Dry Biomass, POWER-TO-GAS Appl., Wiley-VCH Verlag GmbH & Co. KGaA; 2012, p. 181–90.

[93] Moioli E, Gallandat N, Züttel A. Parametric sensitivity in the Sabatier reaction over Ru/Al2O3 – theoretical determination of the minimal requirements for reactor activation. React Chem Eng 2019;4:100–11. https://doi.org/10.1039/C8RE00133B.

[94] Schlereth D, Hinrichsen O. A fixed-bed reactor modeling study on the methanation of CO2. Chem Eng Res Des 2014;92:702–12. https://doi.org/10.1016/J.CHERD.2013.11.014.

[95] Nguyen TTM, Wissing L, Skjøth-Rasmussen MS. High temperature methanation: Catalyst considerations. Catal Today 2013;215:233–8. https://doi.org/10.1016/j.cattod.2013.03.035.

[96] El Sibai A, Rihko Struckmann LK, Sundmacher K. Model-based Optimal Sabatier Reactor Design for Power-to-Gas Applications. Energy Technol 2017;5:911–21. https://doi.org/10.1002/ente.201600600.

[97] Bremer J, Rätzer K, Sundmacher K. CO2 methanation: Optimal start-up control of a fixed-bed reactor for power-to-gas applications. Aiche J 2017;63:23–31. https://doi.org/10.1002/aic.

[98] Sun D, Khan FM, Simakov DSA. Heat removal and catalyst deactivation in a Sabatier reactor for chemical fixation of CO 2 : Simulation-based analysis. Chem Eng J 2017;329:165–77. https://doi.org/10.1016/j.cej.2017.06.160.

[99] Götz M, Lefebvre J, Mörs F, McDaniel Koch A, Graf F, Bajohr S, et al. Renewable

Power-to-Gas: A technological and economic review. Renew Energy 2016;85:1371–90. https://doi.org/10.1016/j.renene.2015.07.066.

[100] Bailera M, Lisbona P, Romeo LM, Espatolero S. Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO2. Renew Sustain Energy Rev 2017;69:292–312. https://doi.org/10.1016/j.rser.2016.11.130.

[101] Specht M, Brellochs J, Frick V, Stürmer B, Zuberbühler U. Synthetic Natural Gas from Coal, Dry Biomass, and POWER-TO-GAS Applications n.d.

[102] Lefebvre J, Götz M, Bajohr S, Reimert R, Kolb T. Improvement of three-phase methanation reactor performance for steady-state and transient operation. Fuel Process Technol 2015;132:83–90. https://doi.org/10.1016/j.fuproc.2014.10.040.

[103] Fukuhara C, Hayakawa K, Suzuki Y, Kawasaki W, Watanabe R. A novel nickel-based structured catalyst for CO2methanation: A honeycomb-type Ni/CeO2catalyst to transform greenhouse gas into useful resources. Appl Catal A Gen 2017;532:12–8. https://doi.org/10.1016/j.apcata.2016.11.036.

[104] Schollenberger D, Bajohr S, Gruber M, Reimert R, Kolb T. Scale-Up of Innovative Honeycomb Reactors for Power-to-Gas Applications – The Project Store&Go. Chemie-Ingenieur-Technik 2018;90:696–702. https://doi.org/10.1002/cite.201700139.

[105] Schirrmeister S, von Morstein O, Fölker H. Innovative large-scale energy storage technologies and Power-to-Gas concepts after optimisation, D2.3 Demonstration plant Falkenhagen commissioned 2017.

[106] Peillex JP, Fardeau ML, Boussand R, Navarro JM, Belaich JP. Growth of Methanococcus thermolithotrophicus in batch and continuous culture on H2 and CO2: influence of agitation. Appl Microbiol Biotechnol 1988;29:560–4. https://doi.org/10.1007/BF00260985.

[107] Nishimura N, Kitaura S, Mimura A, Takahara Y. Cultivation of thermophilic

methanogen KN-15 on H2-CO2 under pressurized conditions. J Ferment Bioeng 1992;73:477–80. https://doi.org/10.1016/0922-338X(92)90141-G.

[108] Luo G, Angelidaki I. Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture. Biotechnol Bioeng 2012;109:2729–36. https://doi.org/10.1002/bit.24557.

[109] Jee HS, Nishio N, Nagai S. Continuous CH4 Production from H2 and CO2 by Methanobacterium thermoautotrophicum in a fixed-bed reactor. J Ferment Technol 1988;66:235–8. https://doi.org/10.1016/0385-6380(88)90054-4.

[110] Seifert AH, Rittmann S, Herwig C. Analysis of process related factors to increase volumetric productivity and quality of biomethane with Methanothermobacter marburgensis. Appl Energy 2014;132:155–62. https://doi.org/10.1016/j.apenergy.2014.07.002.

[111] Burkhardt M, Koschack T, Busch G. Biocatalytic methanation of hydrogen and carbon dioxide in an anaerobic three-phase system. Bioresour Technol 2015;178:330–3. https://doi.org/10.1016/j.biortech.2014.08.023.

[112] Power-to-Gas die Potentialanalyse Power-to-Gas mit biologischer Methanisierung n.d. https://www.microbenergy.de/dienstleistungen/power-to-gas.

[113] Electrochaea employs a patented process to convert electricity and carbon dioxide into methane 2020. http://www.electrochaea.com/technology/.

[114] THE FIRST METHANE HAS BEEN PRODUCED IN THE BIOCAT PROJECT 2020:2–4. https://biocat-project.com/news/the-first-methane-has-been-produced-in-the-biocat-project/.

[115] Leuchtturmprojekt bei Limeco Bau der schweizweit ersten industriellen Power-to-Gas-Anlage Kooperationspartner n.d. https://www.limeco.ch/de/blog/leuchtturmprojekt-bei-limeco-schweizweit-erste-industrielle-power-to-gas-anlage.

[116] Moioli E, Gallandat N, Züttel A. Parametric sensitivity in the Sabatier reaction over Ru/Al2O3 – theoretical determination of the minimal requirements for reactor activation. React Chem Eng 2019;4:100–11. https://doi.org/10.1039/C8RE00133B.

[117] Thema M, Bauer F, Sterner M. Power-to-Gas: Electrolysis and methanation status review. Renew Sustain Energy Rev 2019;112:775–87. https://doi.org/10.1016/j.rser.2019.06.030.

[118] Götz M, Lefebvre J, Mörs F, McDaniel Koch A, Graf F, Bajohr S, et al. Renewable Power-to-Gas: A technological and economic review. Renew Energy 2016;85:1371–90. https://doi.org/10.1016/j.renene.2015.07.066.

[119] Lecker B, Illi L, Lemmer A, Oechsner H. Biological hydrogen methanation – A review. Bioresour Technol 2017;245:1220–8. https://doi.org/10.1016/j.biortech.2017.08.176.

[120] Wulf C, Linssen J, Zapp P. Power-to-gas-concepts, demonstration, and prospects. Hydrog. Supply Chain Des. Deploy. Oper., Christina Wulf; 2018, p. 309–45. https://doi.org/10.1016/B978-0-12-811197-0.00009-9.

[121] Gantenbein A, Witte J, Biollaz SMA, Kröcher O, Schildhauer J. Flexible Application of Biogas Upgrading Membranes for Hydrogen Recycle in Power-to-Methane Processes. Chem Eng Sci 2020:116012. https://doi.org/10.1016/j.ces.2020.116012.

[122] Thunman H. GoBiGas demonstration – a vital step for a large-scale transition from fossil fuels to advanced biofuels and electrofuels. 2018.

[123] Thunman H, Seemann M. The gobigas plant. Elsevier Inc.; 2019. https://doi.org/10.1016/B978-0-12-815554-7.00017-9.

[124] Vázquez FV, Koponen J, Ruuskanen V, Bajamundi C, Kosonen A, Simell P, et al. Power-to-X technology using renewable electricity and carbon dioxide from ambient air: SOLETAIR proof-of-concept and improved process concept. J CO2 Util 2018;28:235–46. https://doi.org/10.1016/j.jcou.2018.09.026.

[125] de Vasconcelos BR, Lavoie JM. Recent advances in power-to-X technology for the production of fuels and chemicals. Front Chem 2019;7:1–24. https://doi.org/10.3389/fchem.2019.00392.

[126] Goeppert A, Czaun M, Jones JP, Surya Prakash GK, Olah GA. Recycling of carbon dioxide to methanol and derived products-closing the loop. Chem Soc Rev 2014;43:7995–8048. https://doi.org/10.1039/c4cs00122b.

[127] Dang S, Yang H, Gao P, Wang H, Li X, Wei W, et al. A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation. Catal Today 2019;330:61–75. https://doi.org/10.1016/j.cattod.2018.04.021.

[128] Moioli E, Mutschler R, Züttel A. Renewable energy storage via CO 2 and H 2 conversion to methane and methanol : Assessment for small scale applications. Renew Sustain Energy Rev 2019;107:497–506. https://doi.org/10.1016/j.rser.2019.03.022.

[129] Bozzano G, Manenti F. Efficient methanol synthesis: Perspectives, technologies and optimization strategies. Prog Energy Combust Sci 2016. https://doi.org/10.1016/j.pecs.2016.06.001.

[130] Rihko-Struckmann LK, Peschel A, Hanke-Rauschenbach R, Sundmacher K. Assessment of methanol synthesis utilizing exhaust CO2 for chemical storage of electrical energy. Ind Eng Chem Res 2010;49:11073–8. https://doi.org/10.1021/ie100508w.

[131] Bellotti D, Rivarolo M, Magistri L, Massardo AF. Feasibility study of methanol production plant from hydrogen and captured carbon dioxide. J CO2 Util 2017;21:132–8. https://doi.org/10.1016/j.jcou.2017.07.001.

[132] Kourkoumpas DS, Papadimou E, Atsonios K, Karellas S, Grammelis P, Kakaras E. Implementation of the Power to Methanol concept by using CO2 from lignite power plants: Techno-economic investigation. Int J Hydrogen Energy 2016;41:16674–87.

https://doi.org/10.1016/j.ijhydene.2016.07.100.

[133] Pérez-fortes M, Schöneberger JC, Boulamanti A, Tzimas E. Methanol synthesis using captured CO 2 as raw material : Techno-economic and environmental assessment. Appl Energy 2016;161:718–32. https://doi.org/10.1016/j.apenergy.2015.07.067.

[134] Deerberg G, Oles M, Schlögl R. The Project Carbon2Chem®. Chemie-Ingenieur-Technik 2018;90:1365–8. https://doi.org/10.1002/cite.201800060.

[135] Roussanaly S, Bureau-Cauchois G, Husebye J. Costs benchmark of CO2 transport technologies for a group of various size industries. Int J Greenh Gas Control 2013;12:341–50. https://doi.org/10.1016/j.ijggc.2012.05.008.

[136] Jiang X, Nie X, Guo X, Song C, Chen JG. Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. Chem Rev 2020. https://doi.org/10.1021/acs.chemrev.9b00723.

[137] Zhong J, Yang X, Wu Z, Liang B, Huang Y, Zhang T. State of the art and perspectives in heterogeneous catalysis of CO2 hydrogenation to methanol. Chem Soc Rev 2020;49:1385–413. https://doi.org/10.1039/c9cs00614a.

[138] Steynberg AP. Introduction to Fischer-Tropsch technology. vol. 152. Elsevier B.V.; 2004. https://doi.org/10.1016/s0167-2991(04)80458-0.

[139] Hanaoka T, Liu Y, Matsunaga K, Miyazawa T, Hirata S, Sakanishi K. Bench-scale production of liquid fuel from woody biomass via gasification. Fuel Process Technol 2010;91:859–65. https://doi.org/10.1016/j.fuproc.2009.09.012.

[140] Bengtsson S. VVBGC demonstration plant activities at Värnamo. Biomass and Bioenergy 2011;35:3–7. https://doi.org/10.1016/j.biombioe.2011.03.034.

[141] Kim K, Kim Y, Yang C, Moon J, Kim B, Lee J, et al. Long-term operation of biomass-to-liquid systems coupled to gasification and Fischer-Tropsch processes for biofuel production. Bioresour Technol 2013;127:391–9.

https://doi.org/10.1016/j.biortech.2012.09.126.

[142] Lee SC, Kim JS, Shin WC, Choi MJ, Choung SJ. Catalyst deactivation during hydrogenation of carbon dioxide: Effect of catalyst position in the packed bed reactor. J Mol Catal A Chem 2009;301:98–105. https://doi.org/10.1016/j.molcata.2008.11.016.

[143] Mai K, Elder T, Groom LH, Spivey JJ. Fe-based Fischer Tropsch synthesis of biomass-derived syngas: Effect of synthesis method. Catal Commun 2015;65:76–80. https://doi.org/10.1016/j.catcom.2015.02.027.

[144] Wang S, Mao D, Guo X, Wu G, Lu G. Dimethyl ether synthesis via CO2 hydrogenation over CuO-TiO2-ZrO2/HZSM-5 bifunctional catalysts. Catal Commun 2009;10:1367–70. https://doi.org/10.1016/j.catcom.2009.02.001.

[145] Gao P, Li S, Bu X, Dang S, Liu Z, Wang H, et al. Direct conversion of CO2 into liquid fuels with high selectivity over a bifunctional catalyst. Nat Chem 2017;9:1019–24. https://doi.org/10.1038/nchem.2794.

[146] Wei J, Ge Q, Yao R, Wen Z, Fang C, Guo L, et al. Directly converting CO2into a gasoline fuel. Nat Commun 2017;8:15174. https://doi.org/10.1038/ncomms15174.

[147] Visconti CG, Martinelli M, Falbo L, Fratalocchi L, Lietti L. CO2hydrogenation to hydrocarbons over Co and Fe-based Fischer-Tropsch catalysts. Catal Today 2016;277:161–70. https://doi.org/10.1016/j.cattod.2016.04.010.