Negative CO_2 emissions from flexible biofuel synthesis: Concepts, potentials, technologies

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ARTICLE INFO

ABSTRACT

This review reports the available technologies for the flexible utilization of biomass towards negative CO_2 emissions and addresses the possibility of coupling bioenergy 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 current 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 captured to achieve 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.

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. However, not all greenhouse gas emissions can completely be avoided at reasonable costs and even negative CO_2 emissions are thought of, to compensate for these residual hard-to-defossilize sectors.

For the defossilisation of energy carriers, the carbon atoms in these hydrocarbons have to originate from non-fossil resources, i.e. taken from biomass or from 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].

For all these reasons, a complete utilization of CO_2 is possible only when sufficient renewable H_2 is available. As this is not always the case, due to the intermittent renewable energy availability, concrete solutions should be envisaged to alternate CO_2 utilization and capture. This goes beyond the current technological development, but such an integrated CO_2 management is needed to ensure a net zero CO_2 economy.

The capture of biogenic CO_2 or the separation of CO_2 from air, followed by injection into exhaust gas fields (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 suggested to achieve negative emissions based on the energetic use of biomass (also referred to as BECCS, Bio-Energy Carbon Capture and Sequestration) by capturing CO_2 from biomass combustion, for example from large wood-based boilers. Another frequently discussed approach is the precombustion carbon capture and sequestration (CCS) of

List of abbreviations		MSR	= Methane Steam Reforming
		PC	= PolyCarbonate Membranes
ASU	= Air Separation Unit	PI	= PolyImide Membranes
BFB	= Bubbling Fluidized Bed Reactor	PSA	= Pressure Swing Adsorption
BtL	= Biomass to Liquid	PsF	= Polysulphone Membranes
CA	= Cellulose Acetate Membrane	PtG	= Power to Gas
CCS	= Carbon Capture and Storage	PtL	= Power to Liquids
CCU	= Carbon Capture and Utilization	PtMeOH	= Power to Methanol
CHP	= Combined Heat and Power Production	PtX	= Power to X
CSTR	= Continuously Stirred Tank Reactor	RT	= Room Temperature
DAC	= Direct Air Capture	RWGS	= Reverse Water Gas Shift Reaction
DFB	= Dual Fluidized Bed Reactor	SAPO	= Silico-Alumino-Phosphate
EF	= Entrained Flow Reactor	SER	= Sorption Enhanced Reforming
FT	= Fischer-Tropsch Synthesis	SOFC	= Solid Oxide Fuel Cells
ICE	= Internal Combustion Engine	SNG	= Synthetic Natural Gas
IGCC	= Integrated Gasification Combined Cycle	TRL	= Technology Readiness Level
MEA	= Mono Ethanol Amine	WGS	= Water Gas Shift Reaction
MeOH	= Methanol	ΔH^R	= reaction enthalpy (kJ/mol)
MMMs	= Mixed Matrix Membranes		
MOF	= Metal Organic Frameworks		

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 paper highlights a third option for negative emissions. 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. 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. It is possible to quantify the amount of CO_2 available in about 20–40% of the original biomass total carbon content [4]. However, this amount of CO_2 is significant for the development of a CO_2-negative energy strategy, thanks to the ease in the 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 paper.

This review is devoted to the description, analysis and comparison of the available technologies and the potential for the flexible integration of bioenergy, Power-to-Hydrocarbon processes and negative emissions. Additionally, the potential for switching between two operation modes is shown: 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 utilization 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 available for energetic exploitation [6].

The structure of the review is represented in Fig. 1. Section 2 describes the existing processes for the recovery of agricultural waste and the energetic valorisation of woody biomass. In Section 3, the existing technologies for the removal of CO_2 from biogas streams are reviewed. These form the first pillar of the flexible use of biomass, because they allow both the production of biomethane and the recovery of biogenic
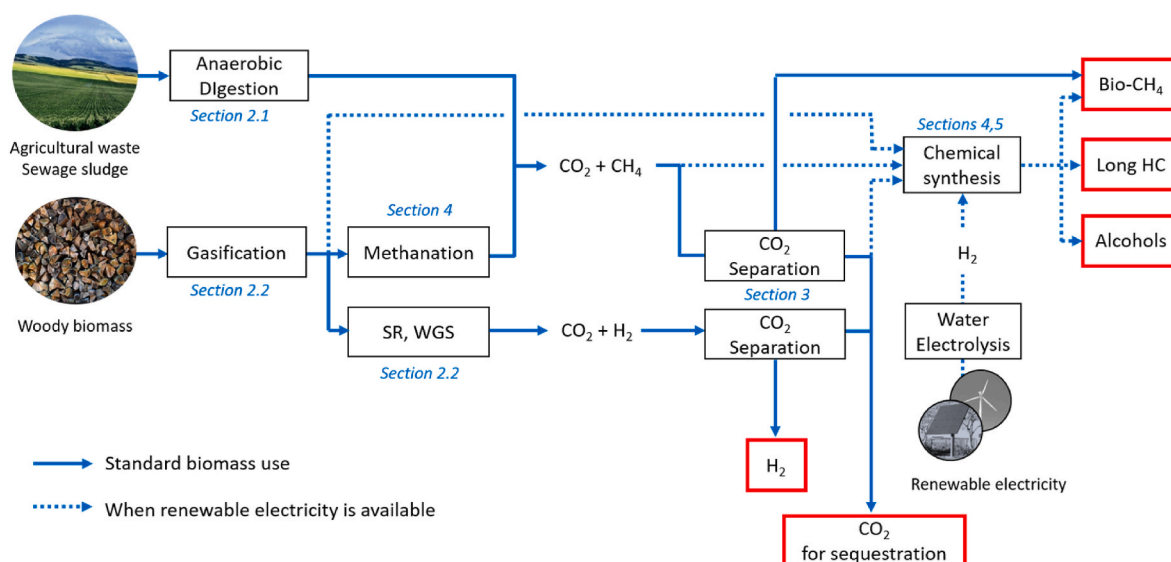

Fig. 1. Structure of the review. (HC = HydroCarbons).

CO_2. Section 4 concerns the direct methanation of biogas, the technology for the valorisation of biogenic CO_2 closest to full maturity. 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. A comparison between the content of this review and other studies available in literature is shown in Table 1. This review compares the technologies for the valorisation of wet and dry biomass and their utilization in the flexible bioenergy production combined with negative CO_2 emissions. This combination is a unique feature of this work, showing how the existing technologies can already be combined to generate significant reduction in the CO_2 footprint of bioenergy applications.

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 anaerobic digestion. 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]. Three different types of feedstock can be distinguished, according to the water content in the biomass: wet, semi-dry and dry [18–20]. Over the last few years, the number of commercially available substrates for the production of biogas has increased considerably, optimizing the utilization of the wastes and making this process economically attractive. Only in Europe, it is possible to account for several hundreds of biogas plants [21]. 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 2. 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 removed from the gas stream with the technologies reported in Section 3 (biogas upgrading). The CO_2, accounting for ca. 40% of the original carbon in the biomass, is readily available to enable negative emissions.

Apart from CO_2, the biogas can contain several other contaminants that must be eliminated to ensure a safe utilization of the bioenergy. These contaminants can be removed with primary (addition of elements to the substrate to avoid contaminant production) or secondary measures (contaminant removal from the biogas). The most relevant impurities are nitrogen, oxygen, water, hydrogen sulphide (H_2S) and

Table 1
Comparison of the content of the present review with previously available reviews concerning biomass utilization and synthetic fuels production (v = topic addressed, x = topic not addressed).

Reference	Anaerobic digestion	Wood gasification	Biogas upgrading	CO_2 methanation	CO_2 to liquid fuels
[7]	v	x	x	x	x
[8]	v	x	x	x	x
[9]	x	v	x	x	x
[10]	x	x	v	x	x
[11]	x	x	v	x	x
[12]	x	x	x	v	x
[13]	x	x	x	v	x
[14]	x	x	x	v	x
[15]	x	x	x	v	x
[16]	x	x	x	x	v
[17]	x	x	x	x	v
This work	v	v	v	v	v

Table 2
Methane content in the biogas and yield of biogas from various sources (elaborated from Ref. [8]). DM = Dry Matter.

Organic source	Methane content in biogas [%]	Yield of biogas production (dm^3/kg dry matter)	Ref.
Agro-food industry waste	65–70	400–700	[22]
Sewage sludge	60–75	200–300	[23]
Municipal green waste	50–60	350–450	[22]

siloxanes [24]. 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 the exhaust gases [25]. Siloxanes decompose to microcrystalline silica (SiO_2) which generates dangerous deposits on the inner surfaces of energy converting units causing abrasion in the moving parts [26]. In primary measures, the formation of H_2S is prevented by adding appropriate materials to 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) [27,28]. Secondary measures include the adsorption of H_2S on iron oxides/hydroxides or on activated carbons [24,29]. These materials are also effective in removing siloxanes from the biogas [25].

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 [30]. These impurities are eliminated with hot or cold gas cleaning technologies, according to the final use of the gasification products [9]. As the C/O/H ratio in the biomass is usually not favorable 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 CO_2 capture. The amount of CO_2 produced in this section accounts 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 [31, 32]. 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.

According to the desired final product (e.g. synthetic natural gas, 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 formation) 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 [33]. Temperature is instead dependent on the gasification technology, as it is a compromise between biomass conversion and process efficiency (i.e. amount of energy in the products vs. heat losses in the combustor). Following these considerations, the optimization of the gasification technology must be conducted according to the specific

process framework.

2.2.2. Available technologies

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

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. Since the residence time in an entrained reactor is low (below 5 s), the operation must be conducted at high temperature (usually above 1300 °C) [30]. The combined effect of low residence time and high temperature limits the production of hydrocarbons so that 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) [38]. 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 system. A standard product gas composition is as follows (in mol. %) [34]: 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. A water-gas-shift (WGS) reactor enhances the production of H_2. H_2 and CO_2 are 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. Entrained flow gasifiers exist at large scale and are provided by various suppliers [31]. 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 [39] and in the BioLiq® [40] projects. This technology is currently employed for the production of methanol/di-methyl-ether (DME) or Fischer-Tropsch (FT) fuels, thanks to the production of a CO/H_2 mixture with appropriate stoichiometric ratio. 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 consists of a 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 3 (BFB Section). As the amount of methane produced is significant, the synthesis of bio-H_2 is challenging with this gasifier type. Methane must be reformed with steam at high temperature in an endothermic reaction. This creates difficulties in the integration with gas cleaning [41], 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, 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 exists since the 1970s [42,43], for example in the methanol synthesis [44,45]. Further examples of this technology are the Foster Wheeler gasifier [46] and the AndritzCarbona/GTI plant [47,48].

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 where the biomass is used as a heat transfer medium between the two sections. In these plants, the two reactors are interdependent and self-adapting. 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) [37,49,50]. Here, 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 bed material
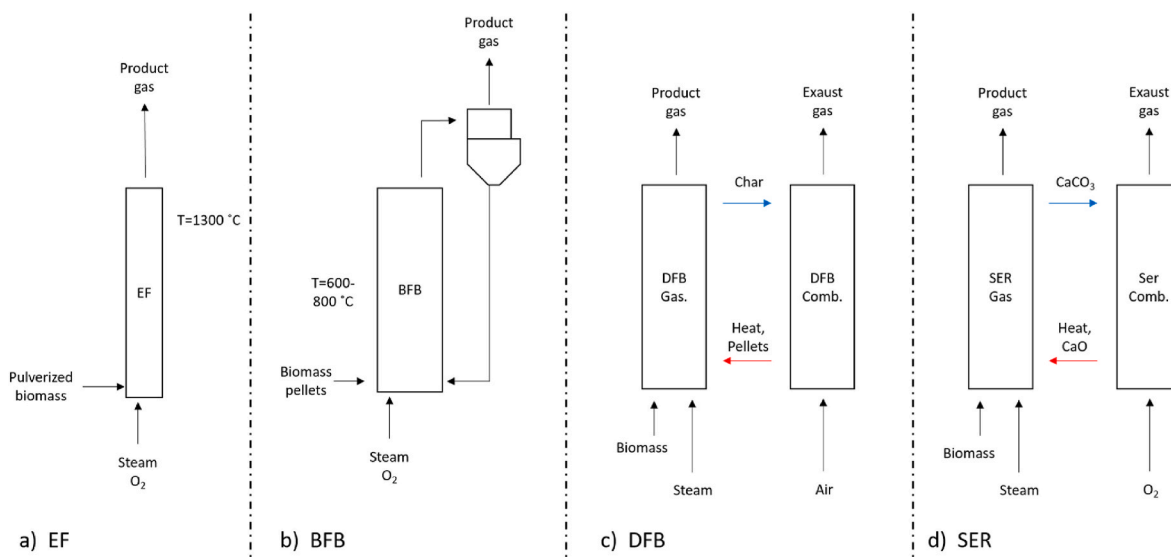

Fig. 2. Detail of the four gasification technologies considered (EF = entrained flow, BFB = bubble fluidized bed, SER = sorption enhanced reformer, DFB = dual fluidized bed).
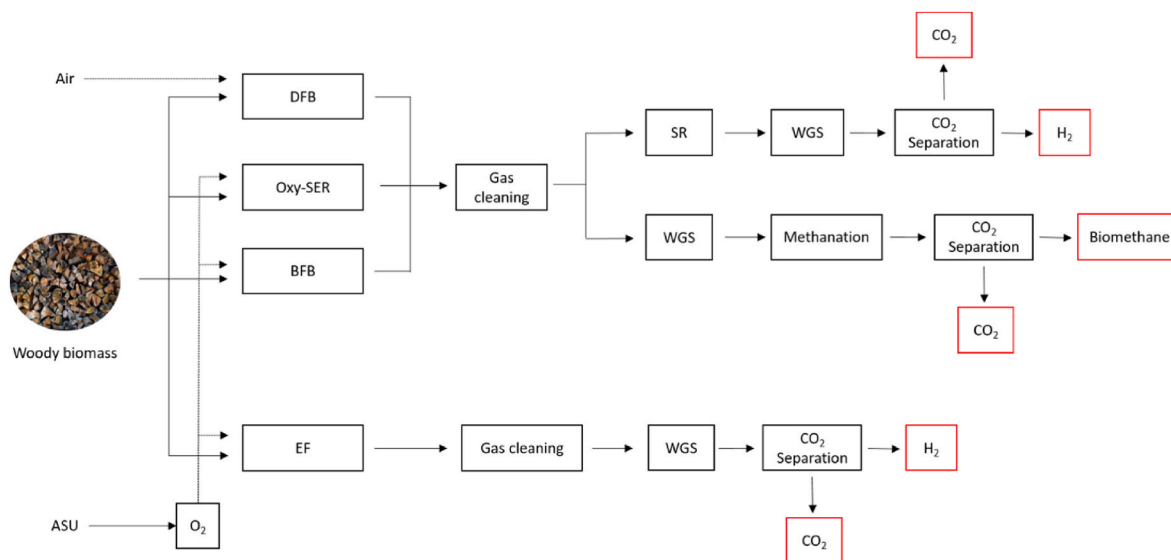
Fig. 3. Overview of the process chains for biomass gasification technologies (DFB = Dual Fluidized Bed, Oxy-SER = oxygen-fed Sorption Enhanced Reformer, BFB = Bubble Fluidized Bed, EF = Entrained Flow, SR = Steam Reforming, WGS = Water Gas Shift).

Table 3
Typical product gas of biomass gasification in the various technologies analysed (EF = entrained flow, BFB = bubble fluidized bed, SER = sorption enhanced reformer, DFB = dual fluidized bed).

Technology	Concentration [mol. %]					Ref.
	H_2	CH_4	CO	CO_2	C_{2+}	
EF	35	–	60	5	–	[34]
BFB	19	17	26	37	1	[35]
(Oxy-)SER	70	15	4	8	3	[36]
DFB	39	10	23	25	3	[37]

is commonly composed of olivine, which is a good heat carrier and a catalyst for the gasification reactions [51]. The typical composition of the product gas is reported in Table 3 (DFB). The amount of H_2 present is doubled than in the case of the BFB, making it more suitable for hydrocarbon synthesis. 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. The main drawback of the DFB as a bioenergy production plant is the difficulty in the CO_2 capture due to the combustion with air. This causes the emission of ca. 1/3 of the C-content of the biomass as CO_2 [36]. The first pilot plant for the DFB technology was installed in Güssing, Austria [37], with a size of 8 MW_{th}. The same concept was used for a further demonstration of a 1 MW bio-SNG production [52]. 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 [53]. 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 [54]. 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. Another type of DFB gasifier is the so-called heat pipe reformer, which was demonstrated at a 500 kW scale [55].

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:

$$CaO + CO_2 \leftrightarrow CaCO_3 \quad \Delta H_0^R = -179 \, kJ/mol \tag{1}$$
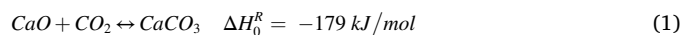
This reaction is highly exothermic and thus enhances the heat supply, while shifting the thermodynamic equilibrium of the WGS reaction. However, lower temperature and longer residence time than the standard gasification are required. Additionally, the spent $CaCO_3$ must be regenerated at high temperature (T > 900 °C). For the SER gasifier, the energy efficiency is thus reduced to ca. 37% [31]. 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 [36,56,57]. A significant amount of CH_4 (ca. 15% vol/vol) is also present, due to the low gasification temperature. The SER technology was validated in Güssing (8 MW_{th}) [58], 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 adjust 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 methane steam reforming (MSR) is the most challenging operation, as the reaction is strongly endothermic and requires high temperature due to 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 [59]. For this reason, the MSR unit can be economically operated only if high temperature heat is available at low cost. EF or SER are the choice reactors for the production of bio-H_2. If the target molecule is bio-CH_4, the design is 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 [60,61]. After removal of the S-species, the final low-temperature WGS (often over Cu/ZnO) and the CO/CO_2

methanation (mainly over Ni) steps are performed. In these last reactors, H_2 from renewable sources can be added to flexibly enhance the bio-CH_4 production. This latter possibility will be explored in detail in Section 4. In general, BFB and DFB are the optimal choices 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]. This process integration consists in the utilization of the waste heat and the hot streams for the pre-heating of cold streams and for the sustainment of endothermic processes. In this way, it is possible to minimize the need for external heat, which may instead become an important cost in the processes. This is essential in the gasification processes, as several gas cleaning and post-treatment steps operating at different temperature are needed. Hence, a minimal size of the processes has to be reached to provide a competitive internal rate of return (IRR) for the investment [62]. However, the collection of large quantities of woody biomass can be challenging and require large transportation facilities, which can be relatively expensive [63]. Some solutions are being developed to avoid this problems, including the intermediate transformation of biomass in a liquid product (bio-oil) [63–65].

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' [66]. Biogas upgrading is a key technology towards the prompt implementation of negative CO_2 emissions, as the CO_2 separation is needed to valorise the methane from biogas and the resulting CO_2 can be compressed and stored with relatively low effort.

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 [67]. The required purity of biomethane changes country by country. However, in almost all the countries, values of CO_2 above 5% are not allowed [68]. Four main technologies are applied for biogas upgrading: water scrubbing, chemical absorption, pressure swing adsorption (PSA) and membranes. The principle of operation of the technologies is summarized in Fig. 4 and the key

performance indicators are summarized in Table 4.

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 exploited 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 [76]. 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 [72]. The efficiency of the system is between 80 and 90% at 10–15 °C [77]. 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). 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

Table 4
Characteristics of the main biogas upgrading technologies (analysis of data from Refs. [67,69]). *RT = Room Temperature.*

|	Water scrubbing	Chemical scrubbing	Membrane separation	Pressure swing adsorption
Electricity demand [kWh/Nm$^3_{BG}$]	0.2–0.3	0.15	0.25	0.2–0.25
Operation temperature [°C]	RT	120–160	RT	RT
Pressure (barg)	5–10	0.1	5–10	4–7
Methane recovery (%)	98	99.96	80–99.5	96
Methane content in upgraded gas (mol %)	>97	>99	>95	>96
Demand for chemicals	no	Yes	no	no
Operating cost (€/Nm$^3_{CH4}$)	0.13	0.17–0.28	0.12–0.22	0.25
Capital cost (€/Nm$^3_{Biogas}$/h)	2500–5000	1500–3000	2000–6000	1500–3000
Market share (%)	44	22	10	21
References	[10,11,67,70]	[10,67,71,72]	[67,72–74]	[10,67,71,75]
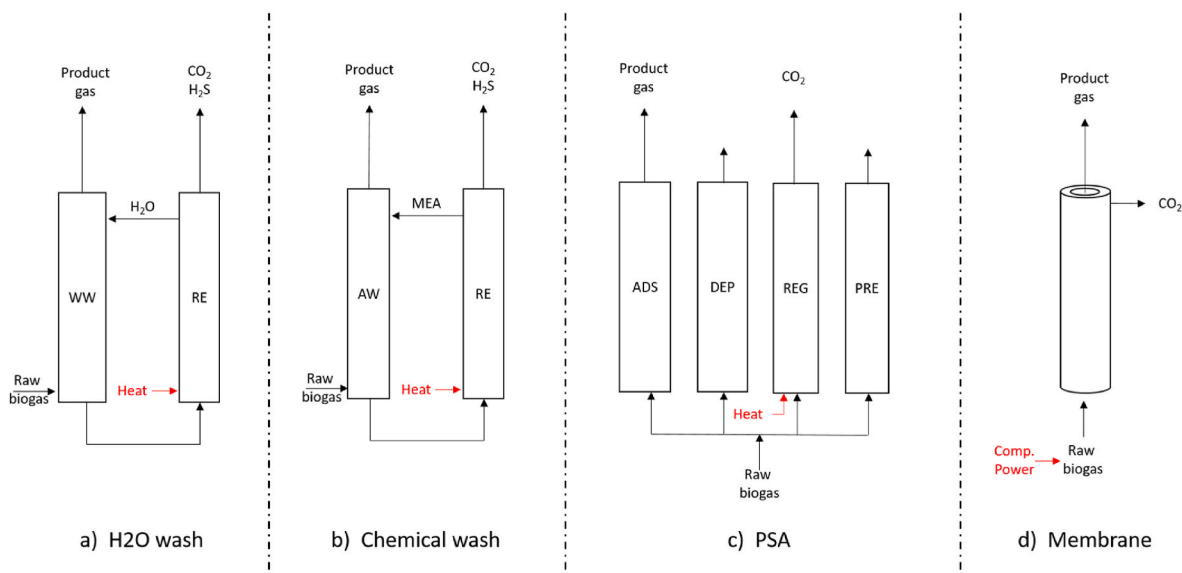
Fig. 4. Working principle of the four main biogas upgrading technologies (WW = water wash, RE = regeneration, AW = amine wash, ADS = adsorption, DEP = depressurisation, REG = regeneration, PRE = pressurisation).

and can be further treated to recover the remaining CH_4 [78]. The amount of water required for this operation is high (0.1–0.2 $m^3 H_2O/Nm^3_{Biogas}$) [10] 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) [11]. The methane losses are around 2% [70]. Energy requirements are mainly due to gas compression, water pumping and regeneration. The capital costs for installation are in the range 2500–5000 €/Nm^3/h for plants with a capacity between 100 and 500 Nm^3/h [10,70]. Currently, about 40% of the biogas plants have a water scrubber installed [67,79].

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) [80]. Typically, amines are used for this reaction. Monoethanolamine (MEA) is the most employed compound, due to high selectivity, high absorption capacity and with low cost [81]. Several other mono- di- and tri-ethanolamines, as well as sterically hindered amines, are also used for biogas upgrading [82]. Alkali salts are also good CO_2 sorbents, but the slow reaction rate and the difficulties in regeneration limit their application in biogas upgrading [11]. 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 [66]. 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 [70]. 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 [70]. The large need of heat for regeneration is one of the main drawbacks of the technology, limiting the market share of chemical scrubbing to ca. 22% [67,79]. 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%) [67]. 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 [10,71,72].

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 [75]. PSA needs a cyclical operation, characterized by periodical loading and regeneration of the sorbent. To obtain a continuous operation, four different units are necessary (Fig. 4d). These operate cyclically the four phases of adsorption, depressurisation, regeneration and pressurisation [10,67].

The materials used for PSA are mainly zeolites or carbon-based adsorbents. Recently, also metal organic frameworks (MOF) and silicoaluminophosphate (SAPO) sorbents have been tested for the process [75,83]. 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 [70]. This corresponds, in the best cases, to a CH_4 recovery of 96%. The market share of PSA is about 20% [79]. The capital cost of a PSA unit is between 1500 and 3000 €/Nm^3/h, the lower value being for a plant with 2000 Nm^3/h capacity [10,71]. The electricity cost (for compression of biogas) is in the range of 0.24–0.6 kWh/Nm^3 [84].

Membrane separation. The membrane separation method 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 [74]. 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 [73]. Inorganic membranes possess a higher mechanical strength, thermal and chemical stability than polymeric membranes, but they are difficult to manufacture, owing to high cost [67]. MMMs aim at combining the advantages of the two, forming a continuous phase with dispersed inorganic molecules [85]. The 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 (Fig. 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 [73]. With a multistage membrane system, 80–99.5% methane recovery is possible, with lower investment and operating cost compared to single stage membranes [86]. 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 [73]. 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) [72]. The market share of biogas upgrading with membrane is currently ca. 10% [79].

3.2. Comparison of the technologies

No technology shows a superior performance over the others. 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 valorisation of biogas into biomethane is especially profitable. 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 valorisation techniques, such as CHP [87,88]. 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 can instead contribute to the development of biomethane production at lower scale, thanks to the lower investment costs. In this sense, especially for chemical absorption and PSA, the market share might 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. A characteristic of rising importance in biogas upgrading is the possibility of combination with synthetic fuels production units.

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)):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{3}$$

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

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

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{4}$$

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

Due to thermodynamic equilibrium, high conversion is possible only at low temperature (below 300 °C). However, the available catalysts are active only above 250–300 °C, which limits the operation window in this interval [89]. At the same time, CO_2 conversion is favoured at high pressure by thermodynamics, but the need of compression increases the energy cost. Hence, most of the technologies operate below 10 bar [13]. 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 [12]. Recently, new interest for the technology raised in the context of energy storage [90]. Here, H_2 is originated from water electrolysis, operated with excess electrical energy [91]. Consequently, 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 [92]. Hence, 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 Sabatier reaction is strongly exothermic. Hence, reaction heat must be efficiently removed from the system, avoiding the operation in a heat transfer limited regime [93,94] and catalyst deactivation due to sintering [95]. 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 [96]. Furthermore, the Sabatier reaction can be performed in biological reactors. The available reactor types are summarized in Fig. 5.

Multistage adiabatic reactor. The multistage adiabatic reactor has first been developed in demonstration experiments in Schwechat and Sasolburg [97]. It is now available as a semi-commercial product (TRL 8) [98]. The technology consists in a series of large vessels, in which the reaction takes place over an appropriate catalyst. The reaction proceeds until reaching the thermodynamic equilibrium [99,100]. The mixture of product and unreacted gas is then cooled, 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 [12]. Haldor Topsoe A/S and Johnson Matthey plc offer processes up to 700 °C, thanks to the use of catalysts that are more resistant to high temperature [101].

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 [102–104]. An optimal profile is 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 [105]. Several demonstration and pilot plants for this technology exist at different scales and TRLs (generally TRL between 5 and 8) [106]. As an example, a multi-tubular reactor was developed by the Zentrum für Solare Wasserstofferzeugung (ZSW) in Stuttgart [107] and applied in a PtG plant in Wertle (Germany) [96,106].

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. The catalyst particles are posed in movement by fluidisation either as gas-solid fluidized 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 [108]. The development of fluidized reactors for PtG applications started relatively recently and specific solutions were tested at the Karlsruhe Institute of Technology (Germany) [106], at the Paul Scherrer Institute (Switzerland) [2], in the EU project
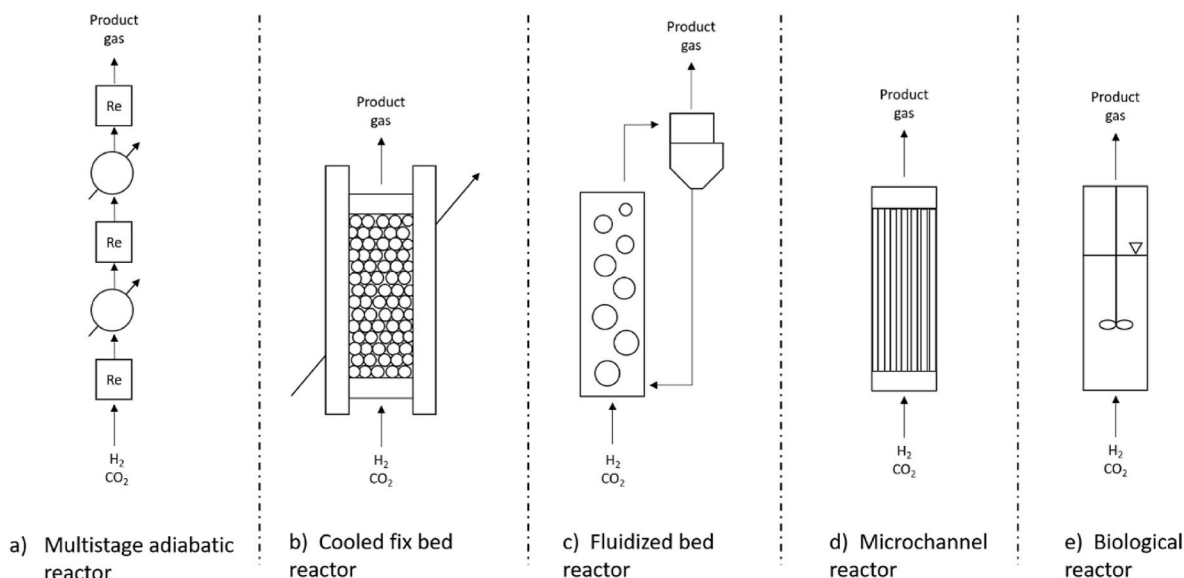

Fig. 5. The available reactor types for the Sabatier reaction.

BioSNG [52], in the French GAYA project [96].

Microchannel reactors. Another strategy to improve the heat transfer in the reactor is the utilization of fixed bed reactors filled with special materials that can improve the heat transfer by conduction (monoliths) [109,110] or by creating a strong radial convection (cross flow structures). Highly conductive metals offer a high radial conductivity between the cooled tube wall and a high axial conductivity, increasing the useable 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 [111].

Biological reactor. The biological methanation reactors are significantly different from the thermo-catalytic reactors. They work at low temperature (up to 80 °C) and ambient pressure with methanogenic microorganism [105]. 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 with high stirring rate are used [112]. The concentration of CO_2 and H_2 must be carefully controlled to avoid pH changes, which are detrimental for the microorganisms [113]. 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 [114]. The reactors developed show variable methane yields [113,115,116]. The best results reported in literature show 98% methane concentration in a trickle-bed reactor, but with low space velocity (0.4 h^{-1}) [117]. Currently, the biological methanation reactors are available as commercial plants and are offered by two providers: Microbenergy [118] and Electrochaea Gmbh [119]. 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 [120], in Solothurn (CH, Store&Go project) [106] and in Dietikon (CH) [121].

4.3. Comparison of the available reactors

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 5 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. 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 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. Catalytic methanation can instead be coupled with processes requiring heat at temperature up to 200 °C. The warm start-up time required (time to produce a gas within the specifications from the warm reactor) is only few minutes for biological reactors, but it sums up to more than 15 min for catalytic reactors. 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. Biological reactors require much bigger volumes than catalytic reactors, due to the difficulties in mass transfer. Among the catalytic reactors, the smallest are 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$_{el}$ [15]. The various reactors here described differ in the degree of maturity. Biological and adiabatic reactors are available at TRL 8–9. 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, 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 Fig. 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 (Fig. 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 Fig. 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 operate flexibly, switching between electricity production, when electricity price is high, and biomethane production, when the electricity price is low. 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. This problem can be partially avoided by installing an H_2 storage system (e.g.

Table 5
Comparison of the main characteristics of the existing CO_2 methanation reactors (TRL = technology readiness level).

| 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 min	15–30 min	15–30 min	Few minutes
TRL	8–9	6–8	6–8	8–9
Consumables needed	Catalyst	Catalyst	Catalyst	Minerals for the broth, power for the mixer
References	[15, 98–100]	[92,93,96, 99,100, 105]	[14,15,92, 96]	[15,105,122, 123]
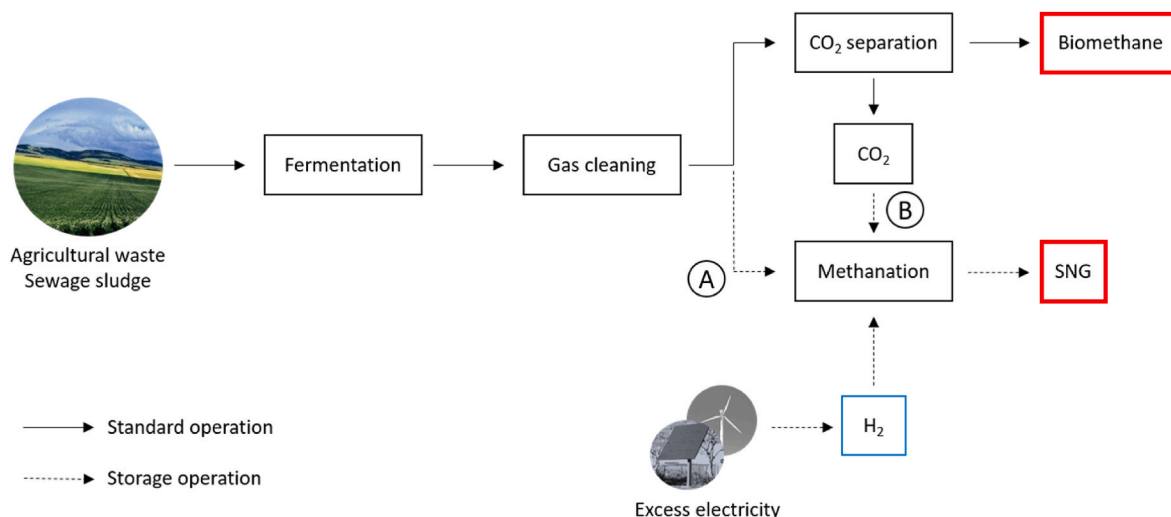
Fig. 6. Process flow diagram of the flexible use of biomass (SNG = Synthetic Natural Gas).

an H_2 tank) to extend the operation time. In the second case, ((B) in Fig. 6), the methanation section operates in 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. Hence, 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 [69]. 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) [124]. When CO_2 is directly obtained and purified from the gas-upgrading unit, it is possible to install a CO_2 storage unit, which increases 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 [106]. 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 usually limited, thus not requiring a large amount of H_2 (from large power plants) for operation.

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 Fig. 2, various gasifiers can be used for the production of a CO_2 neutral SNG. In the post-treatment of gasification, it is possible to focus on the production of biomethane, optimizing the energy yield of the biomass [9]. In this case, the process can be adapted to the flexible use of this biogenic gas, involving the utilization of H_2 produced from renewable resources (e.g. electrolysis) to increase the CO and CO_2 conversion, as shown in Fig. 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 in the methanation reactor, producing further SNG. In this sense, the gasification plant operates both as a biomethane 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 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 large amount of units necessary to clean and reform the gasification products require a careful heat and process integration, which can be performed in a convenient way only in large-scale plants. For this reason, only plants above 100 MW_{prod} may result profitable [125]. 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
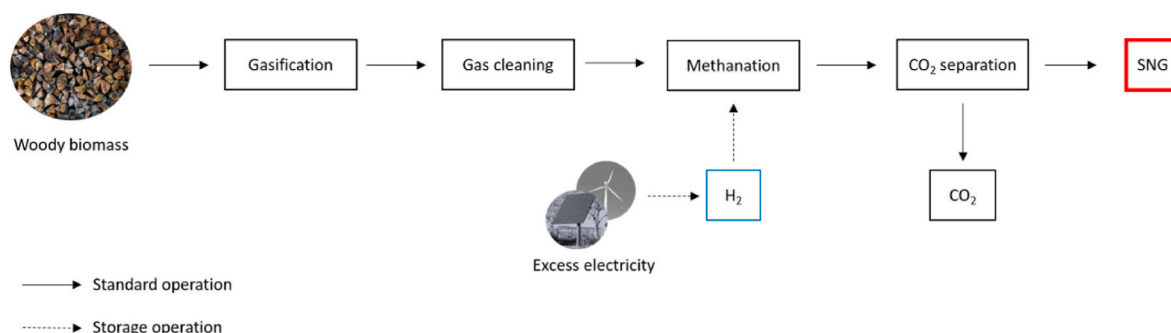

Fig. 7. Flexible use of wood for biomethane production and energy storage (SNG = Synthetic Natural Gas).

preventing the geographically uniform development of the technology [63]. 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 [31] and the GoBiGas project in Sweden [126]. 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 [125]. It is therefore evident that the biomass availability is the key for the further development of the technology.

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

Apart from SNG production, biomass valorisation can be coupled with other PtX processes. Particular interest is linked to the production of liquid fuels, thanks to the easy storage. Furthermore, they can be reconverted in electricity at any time using the standard power plants [127]. Several target molecules can be the object of PtX [128] and biomass valorisation strategies [9]. 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 [129, 130]. MeOH can also be used as a feedstock for the production of DME, which is an optimal diesel substitute [9].

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

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{5}$$
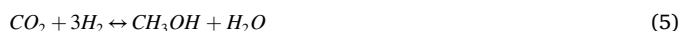
$$\Delta H_R^0(298\ K) = -49.5\ \frac{kJ}{mol}$$

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$_2$O$_3$ catalysts (250–300 °C), is low [131]. For this reason, the commercial processes use high pressure and large recycle streams [132]. 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 [133]. The current technologies can be employed in the PtMeOH process only by implementing an effective process integration at large scale (>50 kt$_{MeOH}$/y) [134,135]. The PtMeOH technology was 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, where a plant producing 5 Mt$_{MeOH}$/y is 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 industrial CO_2 [136]. An interesting example of flexible methanol production comes from the Carb2Chem project that focuses at the production of methanol from steel mill gases [137]. 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. The PtMeOH technology is thus currently at TRL 6–7 [136].

For what concerns the methanol production from biomass resources, some suggestions according to the available demonstrations can be derived. As the currently available technology can be profitable only at large scale, this can be employed only with large supply of biomass. It is possible to imagine the coupling of wood gasification and methanol production, if cheap electricity is available on site [135]. 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.

The methanol production at lower scale is not feasible with the current technology due to the incidence of compression costs [136]. 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 [138].

5.2. Hydrocarbons

Higher hydrocarbons can be synthesized from syngas in the Fischer-Tropsch (FT) synthesis. FT has been developed starting from coal gasification or from natural gas [139] but also demonstration plants from biomass exist [140–142]. 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:

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

$$nCO_2 + (3n+1)\ H_2 \leftrightarrow C_nH_{2n+2} + 2nH_2O \tag{7}$$
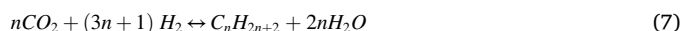
As mentioned in Section 2.2, the gasification process can be tailored for this synthesis, obtaining an optimal CO/CO$_2$/H$_2$ ratio. However, general CO:H$_2$ ratios obtained from biomass can be lower than the required 1:2, down to 0.7:1 [143]. This can be in part solved by use of Fe-based catalysts, which are active in the WGS reaction [144]. 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. The reaction CO_2 to liquid fuels is challenging and the various catalytic technologies are being validated only at lab scale (TRL 1–4) [145–147]. 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 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 non-selective and show low conversion [148]. 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 Fig. 8 can be operated integrating energy storage and hydrocarbon production.

6. Conclusions

In this review, the available technologies for the flexible employment of biomass as a resource to build the future energy system were analysed. These enable two alternative operations: storage of renewable energy or the implementation of negative emissions. 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 were studied. Furthermore, it was underlined how biomass utilization 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
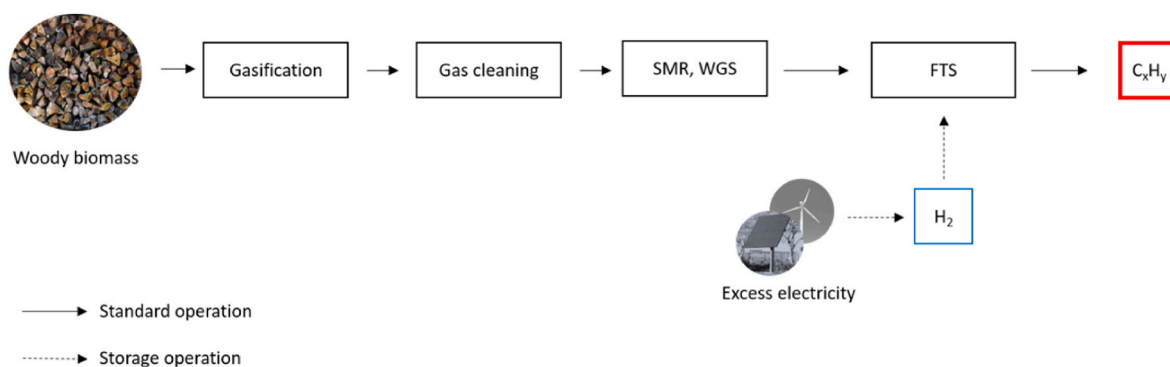
Fig. 8. Process flow diagram of the BtL/PtG hybrid process. (SMR=Steam Methane Reforming, WGS=Water Gas Shift, FTS= Fischer-Tropsch Synthesis).

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. It was 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. This can be forecasted in the long-term perspective (after 2030–2040) when a large production of renewable energy in summer is expected. In a shorter perspective, the availability of energy for synthetic fuel production can be envisaged also in the context of decentralized energy production, where the grid injection may not be possible or economically convenient. Biogenic CO_2 is hence a reliable and continuous source of carbon for the energy system, generating an efficient and flexible coupling of the electric grid with the gas and fuel networks. 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 utilization 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. 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, large 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.

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.

Declaration of competing interest

Acknowledgements

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