

# Power to methane

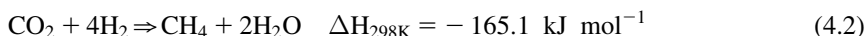
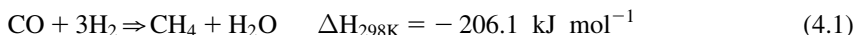
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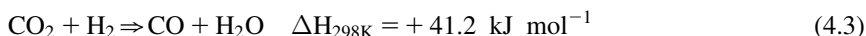
Injecting synthetic methane into existing natural gas pipelines is probably the closest solution to obtain a vast decarbonisation of the energy system. As shown in Fig. 4.1, this solution is suitable to store large quantities of energy and for a long time (hourly to seasonal storage). Therefore it allows to solve the problem of storing a large amount of energy, which is the main obstacle to a greater diffusion of systems based on renewable sources.

The production of synthetic methane involves the methanation of a carbon source using hydrogen. Methanation is an exothermic process that combines hydrogen and carbon oxides generating methane and water, according to reactions (4.1) and (4.2):

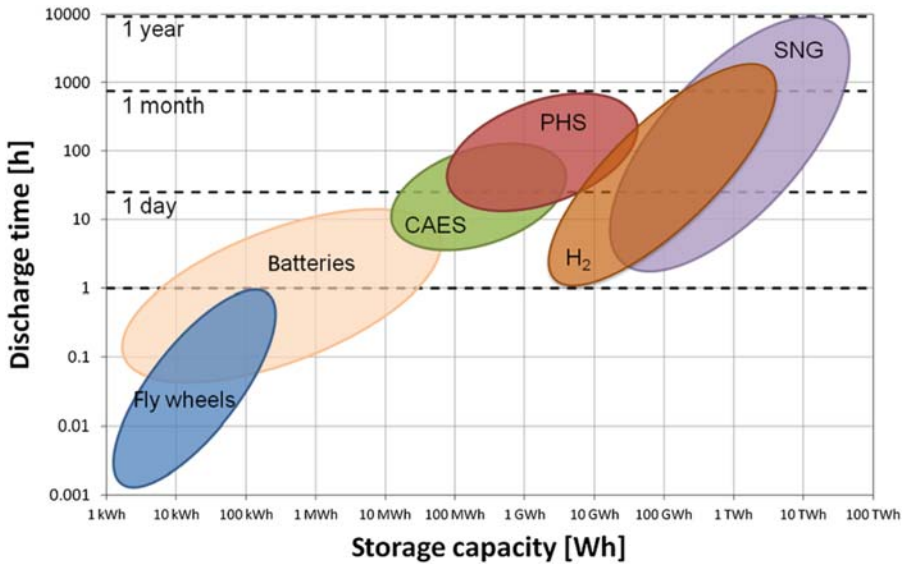


This process has already been used downstream of coal gasification to obtain a gas with a calorific value higher than that of the syngas produced. In fact, hydrogen and carbon monoxide, which are the main components of the syngas produced by coal gasification, have a net combustion enthalpy of 241.8 and 283 kJ mol<sup>-1</sup> respectively, whereas for methane it is 802.6 kJ mol<sup>-1</sup> (Perry and Green, 1998).

Actually, reaction (4.2), called Sabatier reaction and discovered in 1902 (Sabatier and Senderens, 1902), proceeds indirectly through the reverse water–gas shift reaction which reduces CO<sub>2</sub> (Stangeland et al., 2017; Ullmann, 1989):



With a view to a profound decarbonisation of the energy and industrial systems, power plants, refineries, steel industry and cement factories are enormous sources of carbon, even too large for current power to methane technologies. Furthermore, the gases emitted by the aforementioned sectors, although characterised by a high concentration of carbon dioxide, also contain substances that could harm the methanation process, for example sulphur, which can deactivate the catalyst.



**Figure 4.1** Comparison among different energy storage systems. CAES, compressed air energy storage; PHS, pumped hydro storage; SNG, substitute natural gas (Schaaf, Grünig et al., 2014).

Other carbon dioxide sources are represented by biomass combustion and syngas and biogas from various organic sources (e.g. from biomass gasification, waste treatment or anaerobic digestion plants), although potentially available in smaller amount if compared to industrial point sources (see Table 4.1).

The syngas produced by gasification of lignocellulosic biomass mainly contains carbon monoxide and hydrogen, usually without particular harmful substances. The presence of monoxide instead of dioxide can be very advantageous: reaction (4.1) is more direct and production of a mole of methane requires only 3 moles of hydrogen. Furthermore, it is possible to gasify biomass using directly hydrogen (hydro-gasification).

Unlike syngas, biogas is mainly made up of methane (50%–70%) and carbon dioxide (30%–50%) and may contain small amounts of sulphur and silicon compounds (Köppel, Götz, and Graf, 2009; Yentekakis and Goula, 2017). Such a biogas can be used directly, possibly after purification, for methanation, or CO<sub>2</sub> can be used downstream of the upgrading process from biogas to biomethane.

Whatever the carbon source is, after water vapour condensation, the resulting gas from the process could be methane containing only a small amount of carbon oxides and hydrogen. Such a gas is usually called substitute of natural gas (SNG). Often it is also referred to as synthetic natural gas, but we personally do not like this second option because synthetic and natural have opposite meanings. From a technical point of view, SNG could be distributed and used to replace natural gas using the same infrastructures and the same energy conversion devices without particular adjustments. This is because its composition easily falls within the composition limits of a natural gas (see Table 4.2). However, in general, the technical specifications required

**Table 4.1** Typical volumetric flows and required power for electrolysis of different carbon sources (Götz et al., 2016).

CO <sub>2</sub> source		Biogas plant	Biomass gasification	Industrial processes	Power plant
Typical feed gas (m <sup>3</sup> h <sup>-1</sup> ) (STP), dry	CO <sub>2</sub>	500	2100	30,000	300,000
	CO	-	2500	-	-
	H <sub>2</sub>	-	4000	-	-
	CH <sub>4</sub>	500	1100	-	-
Additional H <sub>2</sub> from electrolysis (m <sup>3</sup> h <sup>-1</sup> )		2000	11,900	120,000	1,200,000
Power demand for electrolysis (MW) (5 kWh m <sup>-3</sup> H <sub>2</sub> )		10	59.5	600	6000
Produced CH <sub>4</sub> (total) (m <sup>3</sup> h <sup>-1</sup> )		1000	5700	30,000	300,000
Produced CH <sub>4</sub> (total) (MW)		11	63	332	3320

STP, Standard temperature and pressure.

**Table 4.2** Typical composition of natural gas (Uniongas, 2020).

Component	Range (mole %)
Methane	87.0–98.0
Ethane	1.5–9.0
Propane	0.1–1.5
Iso-butane	Trace–0.3
Normal-butane	Trace–0.3
Iso-pentane	Trace–0.04
Normal-pentane	Trace–0.04
Hexanes plus	Trace–0.06
Nitrogen	0.2–5.5
Carbon dioxide	0.05–1.0
Oxygen	Trace–0.1
Hydrogen	Trace–0.05
Sulphur	Trace–0.002
Properties	Range (MJ m <sup>-3</sup> )
Gross heating value, dry basis	36.0–40.2
Wobbe number	47.5–51.5

for the injection of SNG are determined by the legislation of each country (Thema et al., 2019).

Two different methanation routes are possible: chemical or biological.

## 4.1 Chemical route

Although from a thermodynamic point of view the methanation process is favoured by low temperatures, these hinder the process from a kinetic point of view. In fact, methanation reactions are characterised by a high activation energy and therefore at low temperatures, the number of reacting particles that have an adequate kinetic energy value is very low and the reaction proceeds very slowly. It is therefore essential to use catalysts that are capable of lowering the reaction activation energy to keep the temperature low and favour the carbon conversion to methane rather than the opposite reaction (methane reforming).

### 4.1.1 Catalysts

The catalysts used in the methanation process are solid (heterogeneous catalysis) and the catalyst is generally deposited on a porous support which has a triple purpose:

- increase the active surface;
- guarantee mechanical resistance;
- prevent the dispersion of the catalyst.

The catalyst choice must take into account two fundamental properties: selectivity and activity, which together determine how effective a catalyst is in promoting a certain reaction without favouring competing reactions. The catalysts that can be used for hydrogenation reactions are, of decreasing activity, ruthenium, nickel, rhodium, palladium and platinum (Gao et al., 2015). Obviously, the choice must also take into account the economic factor and Table 4.3 shows the current (18 November 2020) price of the mentioned metals.

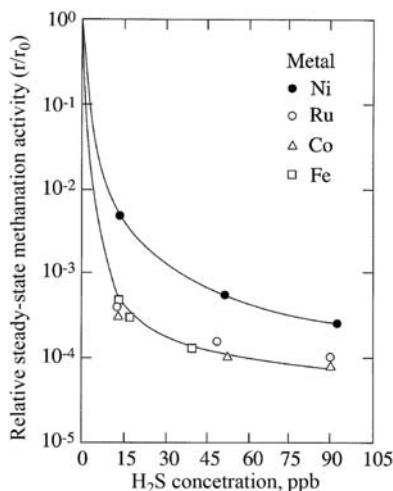
Nickel is the most used catalyst because, in addition to being the least expensive and showing a good activity, it is also endowed with a remarkable selectivity towards the methanation reaction (Martínez et al., 2019).

It is also important to define the shape, size and degree of porosity, characteristics that are related to the type of reactor.

The typical unsupported catalyst is Raney nickel, which is produced by treating a nickel–aluminium alloy with concentrated sodium hydroxide. The hydroxide

**Table 4.3** Cost of metals used as catalysts (Infomine, 2020).

	Pt	Rh	Pd	Ru	Ni
€ per kg	28 €/kg	441,500	70,519	8047	13.27



**Figure 4.2** Effect of H<sub>2</sub>S concentration on the catalytic activity of Ni and other metals. Reaction conditions: 100 kPa, 400°C; 1% CO + 99% H<sub>2</sub> for Co, Fe and Ru; 4% CO + 96% H<sub>2</sub> for Ni (Bartholomew, 2001).

causes the dissolution of aluminium so that the residual copper takes on the appearance of a metal sponge with an extremely fine porous structure and, therefore, with a high specific surface.

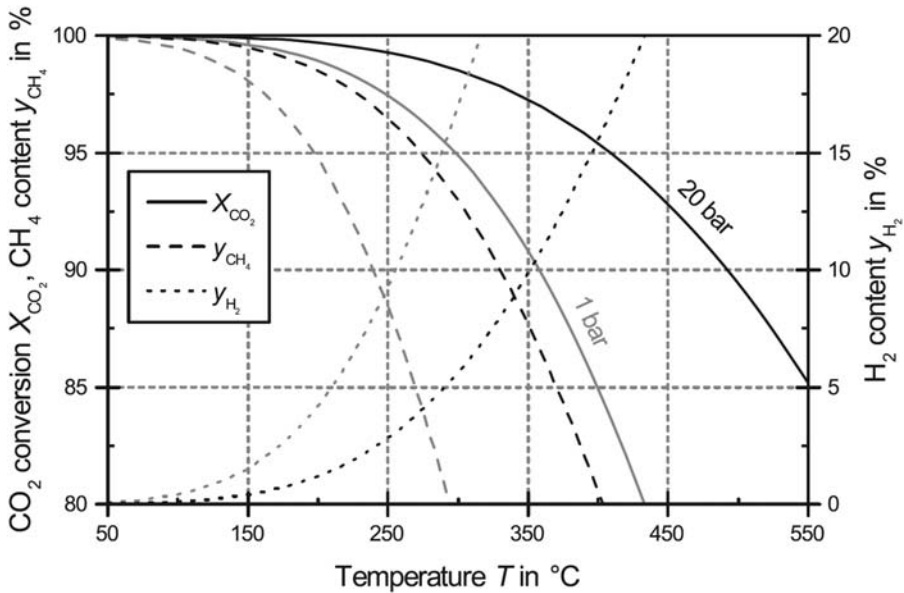
In the case of supported catalyst, however, it is deposited, often in the form of nanoparticles, on porous substrates of alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>) or zeolites, minerals consisting of aluminium and silicon oxides.

Although the catalyst does not participate in the overall reaction, its activity tends to decrease over time with a consequent reduction in the reaction rate. This fact involves the need for catalyst periodic replacement and, consequently, an additional expense that further strengthens the choice of nickel.

However, nickel is particularly subject to poisoning by sulphur compounds. These are obviously not present if pure carbon dioxide is used, but they can be present in case of methanation of a biogas or a syngas. Fig. 4.2 shows how the reaction rate decreases as the presence of sulphur increases. Therefore it is necessary that the feed gas has an overall sulphur content of less than 1 ppm (Bartholomew, 2001; Bartholomew, Agrawal, and Katzer, 1982). Fixed-bed reactors, due to the high temperatures reached, also suffer from the presence of hydrocarbons heavier than methane which can decompose forming coke deposits which deactivate the catalyst (Bartholomew, 1982; Gao et al., 2012).

#### 4.1.2 Operational parameters

Besides the low tolerance against the presence of those impurities, a problem could consist in temperature fluctuations when the process is subject to variability in feed flows, since the latter can cause a drift or a cooling down of the reaction



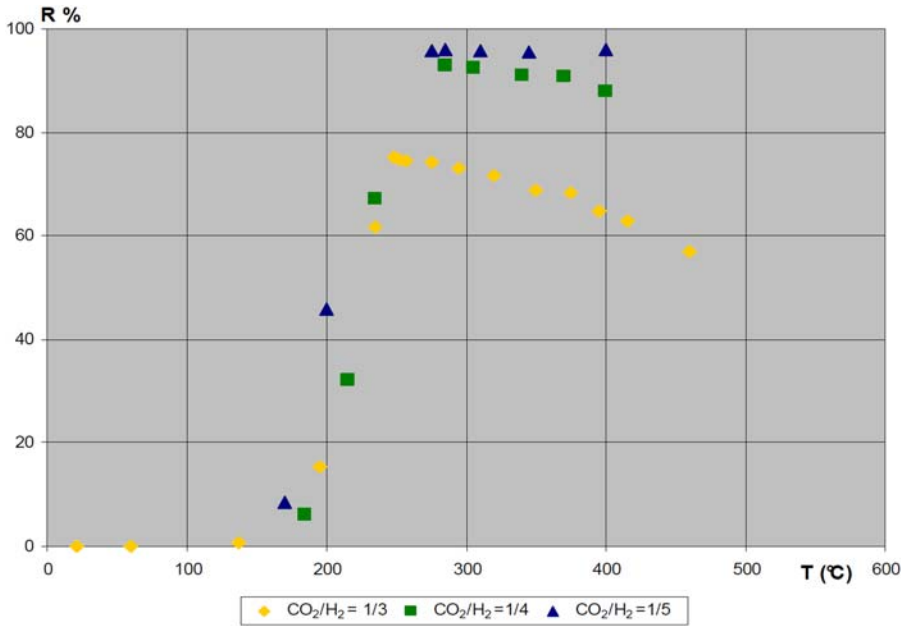
**Figure 4.3**  $CO_2$  methanation: equilibrium conversion and  $H_2$  and  $CH_4$  content for stoichiometric feeding (Götz et al., 2016).

(Bailera et al., 2017; Götz et al., 2016). However, Lefebvre et al. (2015) have shown that the load changes limiting factor is more related to the process control system than to the process itself.

Another parameter that affects the reaction progress is pressure. Since both reactions (4.1) and (4.2) take place with a reduction of molecules, a high pressure is usually adopted. Fig. 4.3 shows the influence of temperature and pressure on the equilibrium conversion of a stoichiometric mixture of hydrogen and carbon dioxide (Götz et al., 2016).

Optimal values of temperature and pressure are respectively in the range  $250^\circ C - 400^\circ C$  and around 30 bar (Foscolo, Gallucci, and Micheli, 2011; Gao et al., 2012).

Finally, the composition of the supplied gas has, within certain limits, considerable importance. Fig. 4.4 shows the methanation yield versus reaction temperature, when the ratio between carbon dioxide and hydrogen in the mixture fed to the reactor is equal to 1:3, 1:4 and 1:5 (Assettati et al., 2010). It is interesting to observe that a temperature around  $200^\circ C$  is needed to start the reaction and that above  $300^\circ C$  the yield starts to drop due to competition from the methane reforming reaction. The stoichiometric ratio between carbon dioxide and hydrogen is 1:4 [see reaction (4.2)] so that for a supply ratio of 1:3 the maximum yield is lower than 80%. At around  $300^\circ C$  there is no significant difference between the yield obtained with a ratio of 1:4 and a ratio of 1:5, whereas for higher temperatures the presence of over-stoichiometric hydrogen slows down the methane reforming reaction and the yield is kept higher.



**Figure 4.4** Methanation yield versus temperature and CO<sub>2</sub>/H<sub>2</sub> supply ratio.

Source: Adapted from Assettati, A. et al. (2010) Sperimentazione di sistemi di trattamento e conversione del syngas. Rome: ENEA.

Being the process exothermic, a very important aspect is heat removal during the process to keep the temperature within its optimal range. With reference to a stoichiometric mixture of carbon dioxide and hydrogen, the heat released by a cubic metre of mixture in standard condition is about 1473 kJ and therefore the heat flux to be removed depends on the gas flow fed to the reactor. A parameter used to normalise the gas flow to the reactor size is the gas hourly space velocity (GHSV):

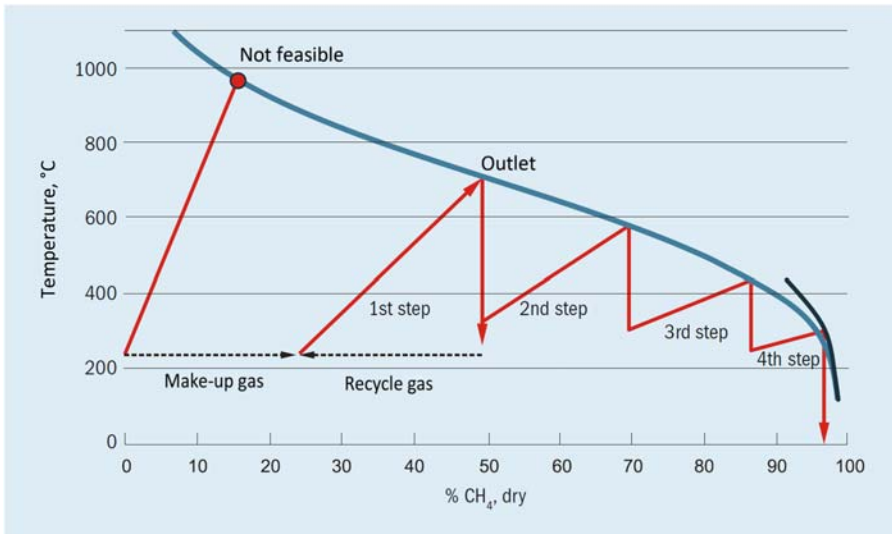
$$\text{GHSV} = \frac{F_{V,g,in}}{V_R} \quad (4.4)$$

where  $F_{V,g,in}$  is the volumetric flow in standard condition of the CO<sub>2</sub> and H<sub>2</sub> stoichiometric mixture, and  $V_R$  is the reactor volume.

### 4.1.3 Reactor structures

The existing methanation reactors can be grouped into the following types:

- fixed bed
- fluidised bed
- three-phase
- structured



**Figure 4.5** Equilibrium curve for methanation process for a specific temperature and pressure (Jensen et al. 2011).

When an adiabatic fixed-bed reactor is used, the temperature increases; this is favourable to the process kinetic since it reduces the need for catalyst but is unfavourable to reaction equilibrium. Moreover, the catalyst is subjected to high temperatures, higher than  $700^{\circ}\text{C}$ , with the risk of cracking or sintering. To obtain a high degree of conversion, a series of reactors with intermediate cooling is required. Due to the larger amount of converted carbon oxides, the first reactor is the one where the most critical operating conditions are reached. For this reason, a partial recycle of its products may be appropriate. Fig. 4.5 shows that, by feeding an adiabatic reactor with a methane-free mixture, the reactor temperature reaches very high values that may be harmful to the catalyst and unfavourable to the chemical equilibrium (Jensen, Poulsen, and Andersen, 2011). By a partial recycle of the reactor products at the inlet, a positive effect is obtained, despite the initial presence of a greater quantity of products which could inhibit the direct reaction. Indeed, the addition of the recycle lowers the reaction temperature, which causes a more favourable effect than the unfavourable effect caused by a higher percentage of methane in the feed. In this way, an almost complete carbon conversion can be achieved with three to four adiabatic reactors.

Such a concept was applied, for example, in the Topsøe recycle energy-efficient methanation process.

To avoid the complexity of a multistage process, a single cooled fixed-bed reactor can be used, from which heat is extracted continuously so that the temperature is maintained at the optimal value. The typical layout of this kind of reactor is a vessel containing several tubes filled with catalyst. The gas flows inside the tubes, whereas the cooling fluid (water, oil or air) flows outside of the tubes. In this case, a single reactor allows to obtain a high rate of conversion. On the other hand, the



heat is extracted at a lower temperature and this reduces the heat recovery efficiency, unless there is the need for low-temperature heat (Bailera et al., 2020; Eigenberger, 1992; Kopyscinski, Schildhauer, and Biollaz, 2010).

A technologically mature alternative to fixed-bed reactors is the fluidised-bed reactor. In this type of reactor, the speed of gases and the size of catalyst particle are such to give the whole the appearance of a fluid. In these conditions, the heat transfer is favoured and the bed temperature is almost uniform, which makes the heat removal simpler than in the fixed-bed reactor (Kopyscinski et al. 2010; Kopyscinski, Schildhauer, and Biollaz, 2011). The disadvantages consist in the need of controlling the gas speed (which must be high enough to maintain fluidisation, but not too high to avoid elutriation of the catalyst), and in the risk of catalyst deactivation due to friction generated by fluidisation (Bartholomew, 2001).

The other two types of reactor are the result of more recent concepts which are still under development.

The three-phase reactor provides for the suspension of fine catalyst particles in a heat-carrying liquid, generally an oil, which gives the mass a high thermal capacity (Held et al., 2020). Therefore as in the case of the fluidised-bed reactor, the heat developed by the reaction can be removed more easily, making the temperature control easier. The main drawbacks of this reactor architecture are the liquid–gas mass transfer resistance and the possibility of liquid decomposition and evaporation (Lefebvre et al., 2015).

Structured reactors are monolithic reactors, that is consisting of a metal mass crossed by channels on whose internal surface the catalyst is deposited (Eigenberger, 1992). Thanks to this metal structure, heat is transferred more rapidly in the radial direction up to two to three orders of magnitude compared to conventional fixed-bed reactors, reducing the possibility of the formation of hot spots (Götz et al., 2016; Held et al., 2020). In case of micro-structured reactors, the pressure drop is also reduced. However, the catalyst deposition inside channels and the replacement of deactivated catalyst is very complex (Liu et al., 2012).

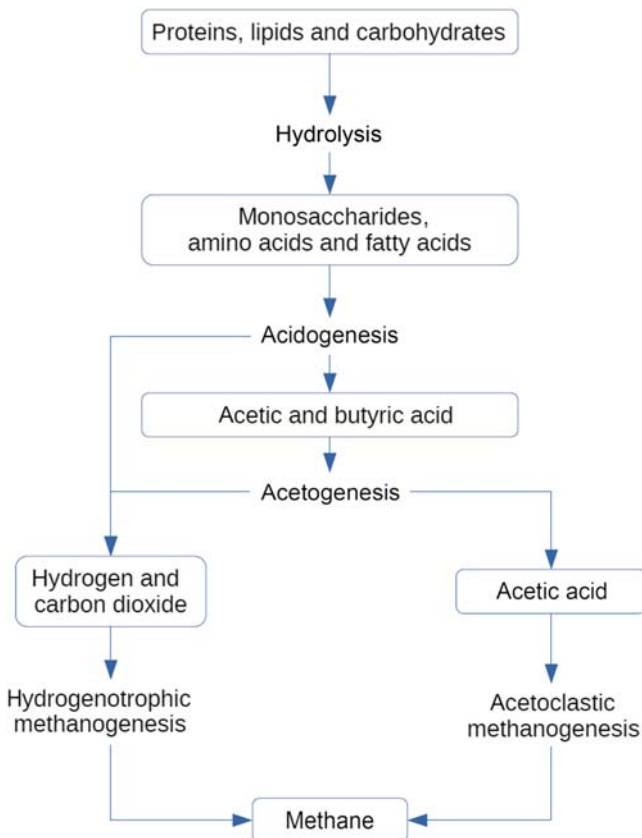
A significant element in terms of cost is the hydrogen storage. Even assuming that there is a constant flow of the carbon donor gas, using the electricity surplus for the production of hydrogen, the availability of the latter varies over time. Therefore to operate the methanation reactor in stationary conditions, it is necessary to have a sufficiently large hydrogen storage, with a consequent increase in both the system complexity and costs.

A methanation reactor that is capable of operating dynamically can eliminate or at least reduce the need for hydrogen storage. On the other hand, this involves critical aspects due to temperature variability when the gas flow varies. In fact, strong temperature changes increase the risk of catalyst cracking or sintering (Bartholomew, 2001). However, several researchers asserted that a change in the gas flow rate is rapidly absorbed also by a catalytic system (González and Schaub, 2015; Götz et al., 2016; Lefebvre et al., 2015). Furthermore, the liquid mass present in the three-phase reactor is able to moderate the temperature variations resulting from load variations. Contrarily, fixed-bed reactors are slower in responding to dynamic fluctuations compared to other reactor types due to their lower temperature control capability, therefore they are less suitable for dynamic operation. However, some authors remark that the catalyst is not significantly affected by load variations (Götz et al., 2016).

While for a fixed-bed reactor a minimum load of 40% is suggested, gas flow rate variations ranging between 25% and 100% were proved to be tolerated by a three-phase reactor (Lefebvre et al., 2015). If the hydrogen flow is insufficient to achieve the minimum acceptable conditions for the reactor operation, it is necessary to switch to standby mode. However, the catalyst tends to oxidise rapidly if exposed to a CO<sub>2</sub> atmosphere (Mutz et al., 2015), which is why it would be preferable for the reactor to contain hydrogen during the standby phase. This implies the availability of a storage system for the carbon donor gas.

## 4.2 Biological route

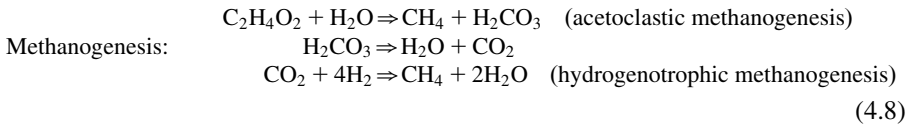
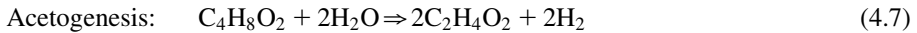
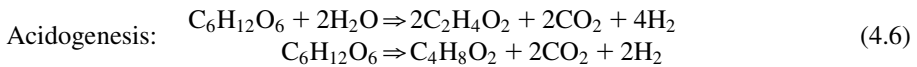
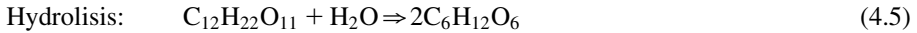
During a biomass anaerobic digestion process, there are four subsequent conversion stages performed by different microorganisms (Fig. 4.6): hydrolysis, acidogenesis, acetogenesis and methanogenesis. During hydrolysis, the biomass, consisting of



**Figure 4.6** Anaerobic digestion process.

complex organic substrates (proteins, lipids and carbohydrates), is attacked by fermentative hydrolytic bacteria (e.g. *Clostridium*) which transforms it into simpler and more soluble compounds such as monosaccharides, amino acids and fatty acids. These compounds are then subjected by fermenting bacteria to an acidogenic fermentation process that transforms them into volatile fatty acids such as acetic acid and butyric acid and starts also to produce carbon dioxide and hydrogen. The generated acids are then further transformed by acetogenic bacteria into acetic acid. Finally, the methanogenic microorganisms generate methane by decomposing acetic acid and combining carbon dioxide and hydrogen (Burkhardt and Busch, 2013; Pavlostathis and Giraldo-Gomez, 1991). An environment that is hostile to methanogenic microorganisms could prevent this last phase and could make it possible to obtain hydrogen.

For example, the chain of reactions leading from sucrose to methane can be the following:



Methanogenesis usually occurs as a final step of a process of decaying organic matter in an anaerobic environment like landfills, swamps, intestines of animals, aquatic sediments, oil fields and sea depths.

In particular, hydrogenotrophic methanogenesis is a process performed by a group of microorganisms (Archaea) in mesophilic or thermophilic conditions (20°C–70°C). These microorganisms obtain energy for their growth from a metabolic route which consumes hydrogen. Since oxygen is toxic to the microorganisms, some oxidised compounds are used to oxidise hydrogen. The simplest compounds utilised by these bacteria are the carbon oxides, which are converted into methane and water.

Since methanogenesis is the final step in the process of biomass decomposition, methanogenic Archaea can tolerate impurities containing nitrogen and sulphur and are not significantly affected by the presence of traces of oxygen although the process is anaerobic (Götz et al., 2016; Seifert et al., 2013). As a consequence, hydrogenotrophic methanogenesis can be applied also as a further step after a process like anaerobic digestion or biomass gasification after providing the adequate amount of hydrogen. However, if the product gas does not fall within the composition specifications suitable for the gas grid, it is necessary to purify it after the methanation.

The conversion efficiency depends on parameters related to the used microorganism (type and concentration) and the reactor (type, operating temperature and

pressure). The substrate acidity is also an important parameter. The conversion efficiency is evaluated in relation to the GHSV (4.4), to the methane concentration in the gas obtained and to the methane formation rate (MFR):

$$\text{MFR} = \frac{\Delta F_{V,\text{CH}_4}}{V_R} \quad (4.9)$$

As with three-phase reactors, it is necessary to take into account the gas–liquid mass transfer resistance and this aspect has a significant influence on the type of reactor. To increase the effective reaction speed, and consequently the MFR, two parameters can be improved: the mass transfer coefficient, which can be increased for example by agitation; and the gas solubility, which can be increased by regulating the pressure (Götz et al., 2016).

Usually, reactors used for biological methanation are continuous stirred tank reactors (CSTRs), in which the reaction takes place in an aqueous solution that is mechanically agitated to favour the gas–liquid mass transfer. In particular, when stirring rates increases, the transfer of hydrogen (much less soluble than carbon dioxide) to the liquid increases (Peillex et al., 1988). A drawback is the power consumption for the agitation (Stone et al., 2017).

The gases are supplied to the vessel from the bottom and rise in the liquid mass coming into contact with microorganisms. Besides increasing gases solubility, working at a higher pressure than atmospheric also increases the contact surface between gases and the Archaea by reducing the size of gas bubbles. On the other hand, a pressure increase causes an increase in CO<sub>2</sub> concentration in the substrate and consequently a reduction in pH: it is therefore necessary to carry out an adequate control of acidity to ensure adequate conditions for the microorganisms (Martin et al., 2013; Nishimura et al., 1992; Wang et al., 2013).

Due to the low reaction rate (GHSV < 10 h<sup>-1</sup>), CSTRs are characterised by a large volume (Bailera et al., 2017). Although this is an advantage from the point of view of system thermal inertia, which allows an easier temperature control, it increases the overall system costs.

As part of a power-to-methane process, it is possible to consider two distinct cases: a simple biomass anaerobic digester or an integrated system comprising the anaerobic digester.

Regarding the last one, the product of anaerobic digestion of biomass is a gas mainly formed by methane and carbon dioxide. Usually, this gas is purified by separating the carbon dioxide to obtain pure methane. This process is called biogas upgrading and the resulting gas is called biomethane. However, the separated carbon dioxide is a waste product, and it could also be converted into methane. Since a reactor in which the methanation process takes place is already available, it is advisable to save money and to avoid carbon dioxide separation by directly supplying the hydrogen flow rate required for the conversion of the excess CO<sub>2</sub> to the reactor. Of course, it is also possible to use the same reactor to convert additional carbon dioxide made available from another source.

About the increase of CO<sub>2</sub> conversion to methane, Götz et al. (2016) reported data from MicroEnergy GmbH which observed a final methane content up to 75%. Other data were reported by Luo et al. (Luo and Angelidaki, 2012; Luo et al., 2012) who experimented carbon dioxide conversion inside a small CSTR at atmospheric pressure and 55°C: 80% of the additional supplied hydrogen allowed a reduction of carbon dioxide from 38% to 15%. Although the advancement of the methanation reaction could be increased by improving the gas–liquid mass transfer of hydrogen, these results prove that converting all the available carbon dioxide is impossible.

By operating biological methanation in a reactor that is specifically dedicated to this process, it is possible to directly use carbon dioxide and hydrogen and to adjust the process parameters in an optimised way for the hydrogenotrophic methanogenic microorganisms. It is also possible to adopt reactors of a different type from CSTR which, although still at an experimental level, could prove to be more efficient.

Using a CSTR with GHSV of 28.7 h<sup>-1</sup>, Nishimura et al. (1992) obtained an MFR of 21.3 h<sup>-1</sup>, with a methane content in the product gas of only 13.4%. Still using a CSTR, in this case with GHSV of 120 h<sup>-1</sup>, a better result was obtained by Seifert, Rittmann, and Herwig (2014): 21.3 h<sup>-1</sup> with a methane content in the produced gas equal to 60%. By reducing the GHSV to 30 h<sup>-1</sup>, the same researchers increased the methane content in the produced gas by up to 85%, while significantly reducing the MFR (Seifert et al., 2014). However, these values are too low for an SNG.

Even changing the reactor type, it seems that high concentration values of methane in the produced gas cannot be reached, except at the expense of production speed.

In fixed-bed reactors, the Archaea cells can be immobilised on a support as a biofilm (Jee, Nishio, and Nagai, 1988), naturally present inside an organic matter bio-filter (Nikiema et al., 2005), or artificially inoculated into an inorganic porous filter (Ganendra et al., 2015).

Also for these reactors, the gases are fed from below, and the liquid, which derives from the production of water from the reaction and from the residue of the nutrient solution that must be periodically supplied to the reactor, is drained from below (Limbri et al., 2014; Nikiema et al., 2005).

Regarding operating parameters, fixed-bed reactors can operate at ambient pressure and temperature (Ganendra et al., 2015; Götz et al., 2016).

Using a fixed-bed reactor, Jee et al. (1988) obtained a methane content of 34% with an MFR of 4.6 h<sup>-1</sup>.

Trickled-bed reactors also contain solid material or filters. In this case, however, there is a continuous circulation of liquid that from the top of the reactor drips down to the discharge. These reactors can operate with both free and immobilised Archaea and produce a gas with a higher methane content, with the same GHSV, compared to fixed-bed reactors (Stone et al., 2017).

In the absence of the agitator action, the mixing between microorganisms and gases is less uniform with the consequence that the GHSV is much lower (Stone et al., 2017). With a trickle-bed reactor it was possible to obtain a methane content of 98%, but with a GHSV of even 0.3 h<sup>-1</sup> (Burkhardt, Koschack, and Busch, 2014).

On the other hand, the energy requirements of both fixed-bed reactors and dropped-bed reactors are very low because they are limited to the feed pump consumption (Thema et al., 2019).

### 4.3 Comparison among available technologies

The first consideration to be made concerns the available technologies level of development: only fixed-bed catalytic methanation is a mature and already commercial technology. Both the catalytic alternatives and biological methanation as a dedicated process are still at a laboratory or pilot-scale experimentation level (Götz et al., 2016).

As can be seen from Table 4.4, due to different operating temperatures, the reaction rate for catalytic methanation is much higher than that found for biological methanation. This has a great influence on the reactor volume and, consequently, on the plant capital cost.

Therefore it can be said that the technology to be adopted depends on the plant size and the carbon source. If the latter is a pure or purified carbon dioxide source, catalytic methanation is to be preferred and the choice may fall on isothermal fluidised-bed or three-phase reactors for smaller sizes, whereas for the large sizes fixed-bed reactors are more suitable. The latter is also preferable in the case of lignocellulosic biomass as a source of carbon. In particular, the adiabatic reactor is convenient when the biomass is subjected to hydro-gasification as the syngas obtained already has a high methane content and no more than two reactors in series are required. Finally, if the biomass is treated by anaerobic digestion, it is possible to inject hydrogen directly into the digester thus operating a biological methanation. As the size increases, it is instead appropriate to separate the digestion phase from that of methanation and the latter can be carried out in a catalytic reactor.

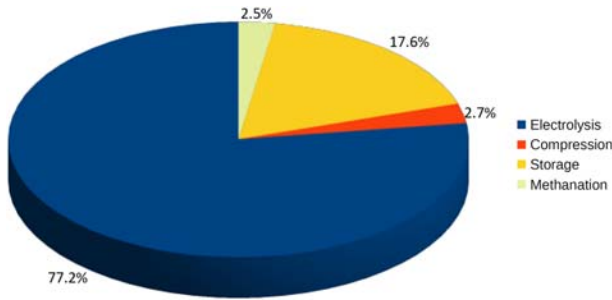
The choice of steady state or dynamic operation depends on cost analysis since it involves the presence and the size of a hydrogen storage. Although a methanation reactor does not work at its optimum during transient operation, its performance depends more on the auxiliary equipment than on the reactor itself. This also entails a certain difficulty in extrapolating the behaviour of a commercial-sized system from the experiments carried out in the laboratory, especially to define the sustainable minimum load below which the reactor must be stopped. Even when the reactor is able to operate with very low flow rates, as in the case of the biological process, it is not economically convenient to go lower a certain minimum load. Götz et al. (2016) report minimum load values ranging from 10% for biological reactors up to 40% for fixed-bed adiabatic reactors.

In the case of a catalytic reactor, the shutdown requires the expulsion of residual carbon oxides, a result that can be obtained by flushing the reactor with hydrogen or inert gas. Furthermore, it must be taken into consideration that at the new start-up energy and time are required to bring the reactor again at the operating temperature. For this reason, if the shutdown duration is limited, it will be preferable to keep the reactor in temperature rather than cool it down.

**Table 4.4** Key parameters of the different reactor configurations of biological and catalytic methanation (Bailera et al., 2020).

	Biological methanation			Catalytic methanation				
	CSTR	FBR	TBR	AFB	CFB	FR	3PR	SR
Temperature (°C)	20–70	20–65	37–55	250–700	250–500	300–400	300–350	250–300
Pressure (bar)	1–3	1	1	5–100	5–100	1–12	20	1–20
Load range (%)	10–100	0–100	0–100	40–100	30–100	50–100	20–100	30–100
GHSV (h <sup>-1</sup> )	10–300	1–30	< 1	< 5000	< 6000	< 60,000	< 1000	< 3000
CH <sub>4</sub> content (%)	5–85	15–90	94–98	> 90	> 90	> 90	> 90	> 90
No. of stages	1	1	1	2–7	1–2	1–2	1–2	1–2
Heat use	Low	Low	Low	High	High	Regular	Regular	Regular
Tolerance to impurities	High	High	High	Low	Low	Low	Regular	Low

*CSTR*, Continuously stirred tank reactor; *FBR*, fixed-bed reactor; *TBR*, trickle-bed reactor; *AFB*, adiabatic fixed-bed; *CFB*, cooled fixed-bed; *FR*, fluidised reactor; *3PR*, three-phase reactor; *SR*, structured reactor.



**Figure 4.7** Cost-sharing of a methanation plant.

From an energy balance point of view, no catalytic reactor needs a stirring system, not even the three-phase reactor, although it contains liquid. In fact, thanks to the operating temperature, hydrogen solubility in the liquid is sufficient even in the absence of agitation. On the contrary, any type of biological reactor needs some stirring device that can be a real stirrer, a feed or a recirculation pump.

Another aspect of the energy comparison concerns the possibility of recovering the heat produced by methanation. In fact, the methanation reactions (4.1) and (4.2) are strongly exothermic, and it is therefore necessary to identify an efficient recovery system to improve the overall process efficiency. In the case of catalytic process, the available heat temperature is above 300°C and this allows the heat to be recovered to produce electricity or steam for industrial or residential use. Conversely, the heat produced in a biological methanation reactor is usually available at a very low temperature, usually around 60°C. Therefore it can only be used for direct heat recovery, for example to heat the anaerobic digestion section in case the methanation phase is separated, or for direct use on-site (i.e. space heating).

Although costs related to electrolysis are rather consolidated, there is limited information on costs related to methanation and misaligned with each other. However, the cost attributable to the methanation unit is very low compared to the other costs of a power to methane plant, as shown in Fig. 4.7, obtained by considering the average of two cases analysed by Götz et al. (2016). The cost by far dominant is the electrolyser one and therefore its correct sizing based on the energy surplus to be accumulated is essential. The cost of the hydrogen storage is also significant, for which reason sometimes it can be convenient to let the methanation reactor work in dynamic behaviour since the higher cost of the latter can be easily compensated by the savings connected to the volume reduction of the hydrogen storage.

Regarding the plant operation, on the one hand the costs of electricity and the carbon dioxide supply have to be considered, whereas on the other hand any revenues from the sale of oxygen and heat recovery should be assessed. It is practically impossible to make a comprehensive assessment without going into the individual specific cases. In fact, in addition to the differences in costs that may exist between one country and another, it must be considered that

- when electricity corresponds to a surplus on the network its cost should be very low, even zero;



- carbon dioxide would certainly have a cost if purchased pure, but its cost could be very low (i.e. as residuals from a biomass treatment plant or industrial carbon sources);
- oxygen has different prices depending on the buyer and required purity;
- heat recovery offers different economic advantages in relation to the product of the recovery itself.

As a consequence, the cost of produced SNG is extremely variable depending mainly on the carbon source, full load hours and electricity cost (Table 4.5). In any case, the SNG cost is higher than the current cost of natural gas and often higher than the cost of biomethane.

Despite this, some fundamental aspects must be taken into account. First of all, the natural gas cost could rise significantly if reserves start to decline or if carbon taxes are applied to fossil fuels. Furthermore, SNG production might reduce the environmental footprint if compared to its fossil alternative (Bargiacchi et al., 2021). Finally, the use of SNG on a large scale can accelerate the transition to a system based on hydrogen as an energy vector, because it allows to build a large

**Table 4.5** Overview of SNG generation costs produced via power to methane.

Full load hours	Assumptions	SNG costs in Eurocent/kWh SNG	Source
1200	80 MW electrical power input	60	Buchholz et al. (2014)
	Energy integration with lignite power plant		
	0–9 ct/kWh electricity	19–50	Müller-Syring et al. (2013)
	5 ct/kWh electricity	27–30	Schaaf, Graf et al. (2014)
	110 MW SNG output		
	0–5 ct/kWh electricity	10–16	Vandewalle, Bruninx, and D’Haeseleer (2015)
10 €/t O <sub>2</sub>			
3000	5 ct/kWh electricity	13.5–17	Schaaf, Graf et al. (2014)
	110 MW SNG output		
	0–3.3 ct/kWh electricity	6.3–21	Brunner and Thomas (2014)
	0–5 ct/kWh electricity	4–8	Vandewalle et al. (2015)
	10 €/t O <sub>2</sub>		
-	Heat and O <sub>2</sub> utilisation	16.5–39.2	E&E Consultant, HESPUL, and Solagro (2014)

SNG, Substitute of natural gas.

Source: Adapted from Götz, M. et al. (2016) Renewable power-to-gas: A technological and economic review, Renewable Energy, 85, pp. 1371–1390. <https://doi.org/10.1016/j.renene.2015.07.066>.

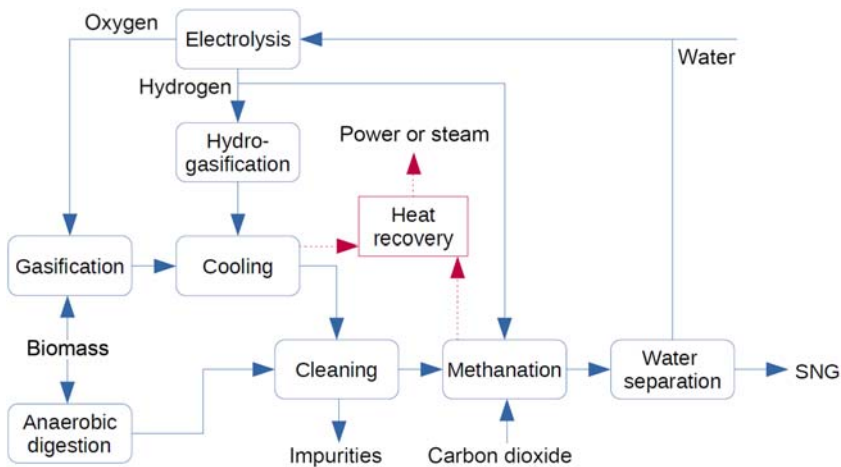
hydrogen production infrastructure and to overcome current bottlenecks for the use of hydrogen on a large scale.

## 4.4 System integration

Methanation process can be applied for direct conversion of carbon dioxide that is captured from other processes or can be integrated in a system including fossil fuels or biomass treatment. Fig. 4.8 shows a generic integrated layout for SNG production from biomass or carbon dioxide. In the latter case, the plant comprises hydrogen production by electrolysis, to which methanation, condensation and separation of water and heat recovery sections are added. Starting from biomass, it is necessary to obtain a gas and three options are schematised: anaerobic digestion, gasification and hydro-gasification.

Actually, the system integration could be even more complex, because the surplus electricity deriving from a renewable energy source could be due to a lack of demand or to a problem of grid instability. Unless there is the possibility of using heat directly, in the first case heat recovery should be used to produce electricity to increase the hydrogen production from the electrolyser. In the second case, the plant also has the task of generating high-quality power for the grid: cogeneration of power and fuel is more efficient than producing fuel alone to be partially used to generate the required power.

Some analyses on the energy balance and life cycle assessment (LCA) have been carried out for a plant based on gasification of hard-wood biomass and devoted to produce a SNG. However for such a SNG, the final hydrogen content is actually much higher than that commercially allowed, but technically it could be distributed



**Figure 4.8** Generic integrated plant layout for SNG production starting from biomass or captured carbon dioxide. SNG, Substitute of natural gas.

using the existing pipeline and used in natural gas-fuelled vehicles (Bargiacchi et al., 2021; Bargiacchi, Frigo, and Spazzafumo, 2018, 2019; Frigo and Spazzafumo, 2020).

In case there is no need for power, hydro-gasification has been considered as the preferable treatment, whereas to cogenerate power the possibility to use oxygen as a gasifying agent has been selected and some different power units have been considered.

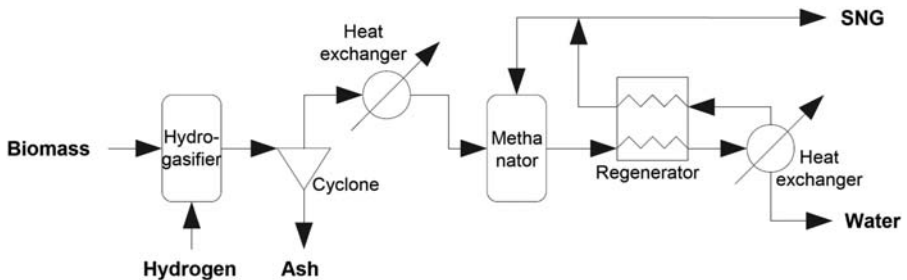
Fig. 4.9 shows the layout with a hydro-gasifier. An over-stoichiometric flow of hydrogen is fed to the hydro-gasifier in such a way that the produced syngas is mainly composed by methane, hydrogen and water, with a small although not negligible amount of carbon oxides. Therefore a subsequent methanation process is required, but only one adiabatic reactor is needed to convert almost completely the residual carbon oxides into methane.

When cogeneration of power is needed, biomass is gasified using part of the produced electrolytic oxygen, and the obtained syngas can be burnt into a power unit, for example a gas turbine or an internal combustion engine. Being further electrolytic oxygen available, oxy-combustion in the power unit offers the advantage to obtain an exhaust gas composed almost exclusively of carbon dioxide and steam, so that almost pure CO<sub>2</sub> can be easily obtained by steam condensation and separation. On the other hand, a problem arises from the high combustion temperature achieved and a temperature moderator is required to replace the role of nitrogen in the air; this issue could be easily solved by a partial recycling of carbon dioxide. Another solution proposed for gas turbine is the water injection. Finally, it is also possible to supply the syngas to a high-temperature fuel cell stack.

In all these cases, all the carbon present in the biomass is converted to carbon dioxide, and the methanation section in the case of adiabatic reactors is shown in Fig. 4.10, requiring only a partial recycle at the entrance of the first methanator.

Due to the reaction exothermicity, a certain amount of heat is available and must be extracted from the different reactors. To optimise the heat recovery, heat exchangers can be divided into two groups, namely at high and at low temperatures. A bottoming Brayton cycle working with air and two pressure levels can be designed and its power can be increased by producing steam to be injected into the high-pressure turbine (Fig. 4.11).

Table 4.6 reports the result obtained from the energy analysis.



**Figure 4.9** Layout of biomass hydro-gasification followed by methanation (Frigo and Spazzafumo, 2020).

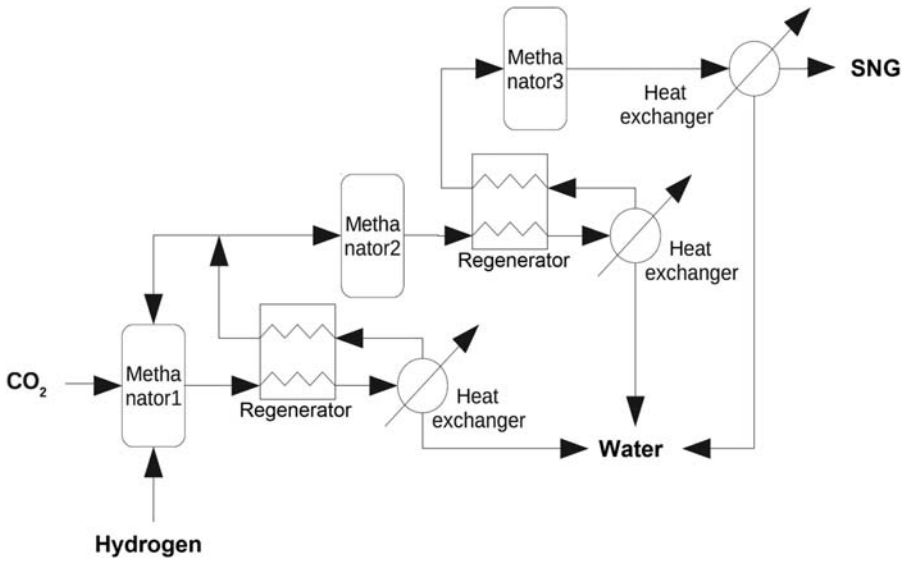


Figure 4.10 Methanation section (Frigo and Spazzafumo, 2020).

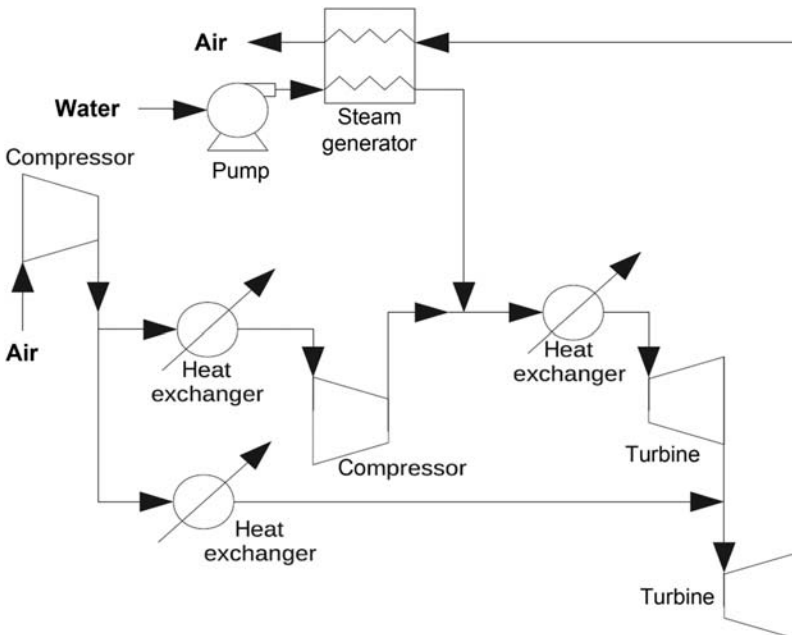


Figure 4.11 Bottoming plant for heat recovery (Frigo and Spazzafumo, 2020).

**Table 4.6** Energy balance (based on HHV).

	Hydro-gasification	Cogeneration
Biomass (kW)	3911	
Electrolysis (kW)	8184	16044
SNG (kW)	8931	8904–8935
Electrical power (kW)	0	1523–2914
Efficiency	73.8%	52.4%–59.4%
Chemical input (biomass)	32%	20%
Chemical output (SNG)	100%	75%–85%

HHV, Higher heating value; SNG, substitute of natural gas.

## 4.5 Environmental impacts of substitute natural gas

As many other synthetic fuels, the environmental impacts of SNG production were investigated by several authors in recent years, by means of LCA methodology. This section does not mean to provide a full, comprehensive state of the art of the environmental assessment of power-to-methane systems, rather to provide relevant references and point out the challenges to be addressed.

Regarding chemical methanation, [Zhang et al. \(2017\)](#) investigated the environmental performance of SNG and power to methane systems using LCA and considering different carbon sources (CO<sub>2</sub> from atmosphere, from cement plant, from coal power plant) as well as different technologies for electricity supply and electrolysis, while using thermochemical methanation. The main result is that the energy mix for electricity production and the CO<sub>2</sub> source dominates the life cycle emissions and therefore the reduction potential of this new technology in comparison with natural gas. On the same topic, [Hoppe, Bringezu, and Thonemann \(2016\)](#) concluded that SNG production from an industrial CO<sub>2</sub> source (in this case from raw biogas separation) in the German scenario saves greenhouse gas emissions if compared to natural gas. On the other, [Sternberg and Bardow \(2016\)](#) argued that the power-to-gas pathways imply higher global warming impact (GWI) and fossil depletion than conventional natural gas even in a 2050 electricity mix while proving promising GWI reduction with the power-to-syngas routes. [Collet et al. \(2017\)](#) compared different scenarios for biogas production with SNG production via power to gas, proving that impacts of power to gas are higher than with biogas upgrading for continuous operation but lower than natural gas impacts.

Regarding SNG production from biomass, [Felder and Dones \(2007\)](#) evaluated the ecological impacts of SNG production from wood with its utilisation in current heating systems and cars. They found that SNG outperforms the oil derivatives and

the fossil natural gas when the consumption of fossil resources is strongly weighted in the assessment. [Tasca et al. \(2019\)](#) performed an LCA of biomethane production from gasification of poplar short rotation forestry wood chips and anaerobic digestion of microalgae biomass. [Skorek-Osikowska, Martín-Gamboa, and Dufour \(2020\)](#) conducted a combined technical, economic and environmental assessment of the production of biomethane from three different pathways: manure fermentation and upgrading, manure fermentation and biogas methanation using renewable hydrogen from electrolysis and biomass gasification with syngas methanation. Both Tasca and Skorek-Osikowska concluded that no solution outperforms the others on all impact categories and that in any case the proposed solutions still need improvements to be economically competitive with natural gas. [Gerber, Gassner, and Maréchal \(2011\)](#) proposed a methodology to integrate LCA in techno-economic models, and they applied it to a thermo-economic model developed for the optimisation of SNG and electricity production from lignocellulosic biomass. Recently, [Singlitico, Goggins, and Monaghan \(2019\)](#) conducted a comprehensive review of LCA papers dealing with the production of biomethane, produced by anaerobic digestion, and SNG, produced by methanation and gasification.

Finally, the layouts mentioned in the previous section were analysed under environmental criteria, selecting global warming potential (GWP), non-renewable cumulative energy demand (CED<sub>nr</sub>) and acidification potential (AP) as the main impact indicators, due to their relevance in the field of hydrogen energy systems ([Bargiacchi et al., 2021](#)). Some methodological aspects were also considered, as the choice of two different functional units (1 kg of SNG and 1 MJ of SNG) and different approaches to address the multifunctionality of such a cogeneration system. Results show that, with all the considered system layouts, SNG production from biomass and renewable electricity presents a significantly lower impact than that of conventional natural gas under GWP and CED<sub>nr</sub>, whereas higher impacts than natural gas ones are obtained under the acidification footprint. The cause of this high impact in AP is mainly associated with the alkaline electrolyser infrastructure and in particular is ascribable to the mining of catalyst metals (nickel and rhodium) for electrodes manufacturing. When total energy in output (SNG + electricity) is considered as the functional unit, these trends of comparison with natural gas are confirmed, with the layout based on hydro-gasification showing an impact lower than the other systems under comparison. Finally, it was found that different methodological choices to deal with the system multifunctionality can affect the ranking between the different technologies under comparison but they did not overturn the overall results in terms of comparison with natural gas.

Overall, although most of the authors proved that SNG has the potential of reducing the overall environmental footprint in the gas sector rather than its fossil alternative, the environmental benefits must be carefully assessed on a case-by-case basis. Some precautions are essential to minimise the environmental impact of an SNG, such as the use of a renewable energy mix for electricity production, a suitable choice of the CO<sub>2</sub> source and a careful choice of the materials to avoid burden-shifts.

## Nomenclature

<b>AP</b>	acidification potential
<b>CED<sub>nr</sub></b>	non-renewable cumulative energy demand
<b>CSTR</b>	continuously stirred tank reactor
<b>F</b>	flow in standard condition
<b>GHSV</b>	gas hourly space velocity
<b>GWP</b>	global warming potential
<b>GWI</b>	global warming impact
<b>LCA</b>	life cycle assessment
<b>MFR</b>	methane formation rate
<b>SNG</b>	substitute natural gas
<b>V</b>	volume

### Subscripts

<b>g</b>	gas
<b>R</b>	reactor
<b>V</b>	volumetric

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