Advanced Review

# Comparison of synthetic natural gas production pathways for the storage of renewable energy

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The production of synthetic natural gas (SNG) to store renewable energy in a chemical energy carrier can be accomplished basically through three main production pathways: the biochemical (biogas upgrade), thermochemical (gasification and synthesis gas upgrade) and electrochemical ('Power-to-Gas') pathway. The technologies applied in these concepts are described and the three pathways are compared in terms of their state of development, efficiencies, and economics. While the biochemical pathway is already established on a commercial scale, the thermochemical and electrochemical routes are still in the pilot-plant phase. Biochemical production of SNG reaches efficiencies in the range of 55–57% but with a potential of above 80%. In comparison, higher efficiencies of up to 70% for the thermochemical pathway are currently expected, with future improvement up to 75%. Electrochemical production achieves efficiencies in the range of 54–60% with expected potential up to 78%. Therefore at the moment the highest efficiencies are given for the thermochemical pathway followed by the electrochemical and biochemical pathways. Economic evaluation is done by comparing specific production costs as well as mean specific investment costs for SNG. Generally speaking, specific production and investment costs decrease with time horizon and increasing scale of the plant. Specific production cost levels in €ct/kWh$_{SNG}$ vary between 5.9 and 13.7 (biochemical), 5.6 and 37 (thermochemical), and 8.2 and 93 (electrochemical). Thus, none of the concepts can compete with today's natural gas prices, but all options are able to provide valuable assistance for a sustainable transition of the energy system. © 2015 John Wiley & Sons, Ltd

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## INTRODUCTION

In 2009, the G8 countries agreed to reduce greenhouse gas emissions by 2050 by 80% or more against 1990 levels.[1] The long-term transition toward a renewable energy based system is the basis for reaching these ambitious goals. Thereby SNG produced from renewable energy sources can play a key role for greenhouse gas reduction as well as in guaranteeing the security of supply by balancing the increasing volatile energy supply of wind and PV. SNG benefits from an existing well-developed infrastructure for storage, distribution, and utilization. Currently, there are 688 underground gas storage facilities in operation at worldwide level with a storage capacity of about 990 TWh in Europe and 1520 TWh in North America, which is in the range of 30–35% of the respective energy consumption per year.[2,3]

Owing to its storage and distribution potential, the natural gas infrastructure allows a decentralized regenerative production of SNG from biomass for flexible utilization in internal combustion engines or highly efficient combined cycle power plants with optional combined heat and power production. In

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the long term, SNG produced via water electrolysis and methanation can also serve as seasonal storage for excess electricity from wind and PV when regenerative supply exceeds demand.[4] Germany is playing a pioneering role in the commercialisation of this so-called Power-to-Gas (PtG) technology due to its ambitious goal of achieving an 80% share of renewables in gross electricity generation by 2050[5] with an expected need for energy storage in the GW range.[6–8] Owing to its high energy density of 1200 kWh/Nm$^3$ (at 200 bar) compared to compressed air with 6.9 kWh/Nm$^3$ or pumped hydro storages with 0.23 kWh/Nm$^3$ SNG is especially suitable for seasonal storage.[9]

Beside conversion to electricity, SNG can also be used for heating or in the mobility sector. Today, natural gas is mainly used for power generation followed by industrial utilization (e.g., chemical industry or iron and steel industry) and household consumption (primarily domestic heating) (Figure 1). Transportation represents only a minor consumer of natural gas although the trend is rising. Power generation from natural gas and biogas has increased dramatically over the last 20 years (Figure 2).

Today there are great differences in global natural gas prices due to the high production of shale gas in the United States resulting in a decoupling of prices from 2009 on (Figure 3). While prices in Europe and Japan have been in the range of 25–40 €/MWh over the past few years, prices in the United States dropped to about 5–15 €/MWh. Therefore, Europe is a market driver for renewable SNG, although standardization of grid injection regulations for SNG is still an issue. Table 1 shows the range of some current requirements in various European countries. Besides the limitations of main gas components like $H_2$ or $CO_2$ the content of contaminants like sulfur is also regulated.

The review provides an overview of sustainable pathways for SNG production and evaluates and compares the three most relevant routes, namely the biochemical, the thermochemical, and the electrochemical pathways in terms of technologies, efficiency, economics, and market maturity.

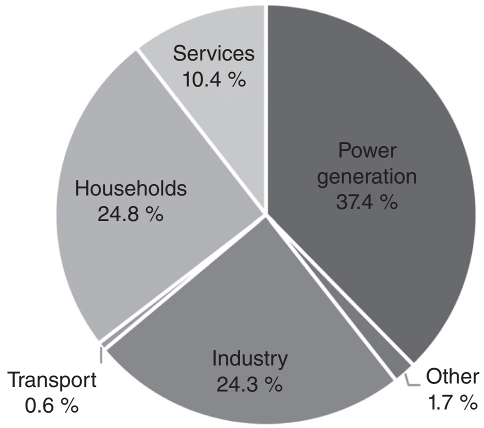

**FIGURE 1** | Natural gas consumption per sector in the EU in the year 2011.[10]

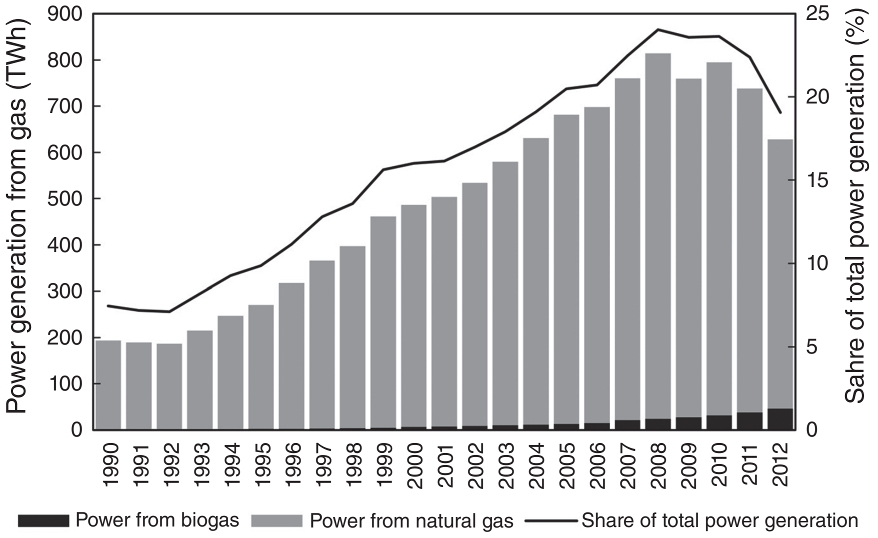

**FIGURE 2** | Historic development of power production from natural gas and biogas in the European Union (own illustration based on Ref 11 for EU 28).

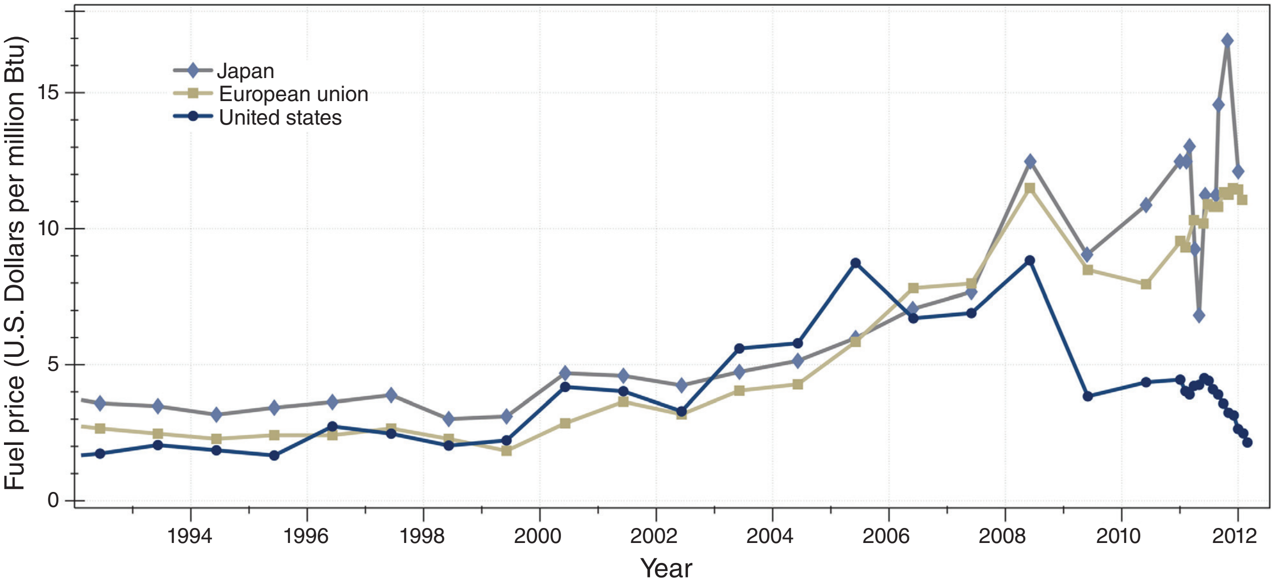

**FIGURE 3** | Natural gas prices in Japan, the European Union and the United States, 1992 to 2012.[12]

**TABLE 1** | Range of Requirements of Various European Countries for Injection in Natural Gas Grid (adapted from Ref 13)

| | Value | Unit |
|---|---|---|
| Wobbe index | 10.5–15.7 | $kWh/Nm^3$ |
| Higher heating value | 8.4–13.25 | $kWh/Nm^3$ |
| Water dew point | $< -60$ to 5 | °C |
| $CH_4$ | >90–97 | % mol |
| $CO_2$ | 2.5–6 | % mol |
| $H_2$ | 0.5–12 | % mol |
| $O_2$ | 0.1–1 | % mol |
| Sulfur (in total) | 10–45 | $mg/Nm^3$ |
| $H_2S$ | 5–10 | $mg/Nm^3$ |

## TECHNOLOGICAL OVERVIEW

The following chapter provides a brief technological overview of the three most relevant pathways to generate grid-injectable SNG:

1. **Biochemical SNG production:** Starting from wet biomass, the most advanced and widely applied method is the biological conversion of biomass via fermentation to biogas. The resulting biogas already consists of about 50–75% methane ($CH_4$) together with a major fraction of carbon dioxide ($CO_2$). By applying a $CO_2$ separation unit, the resulting gas, mainly methane, can be fed into the natural gas (NG) grid as SNG.
2. **Thermochemical SNG production:** The second pathway for the generation of SNG is the thermochemical pathway consisting of biomass gasification and a subsequent gas cleaning and catalytic synthesis to methane with final upgrading of the raw-SNG for grid injection.
3. **Electrochemical SNG production:** The third option is the production of hydrogen from excess electricity generated by renewable sources via water electrolysis with subsequent methanation with $CO_2$ (e.g., from biogas upgrading plants).

The three options, including process steps, important framework conditions and process parameters as well as specifications are explained in the following.

## BIOCHEMICAL SNG PRODUCTION

Biochemical SNG production via fermentation of wet biomass is the most mature technology from an application point of view. The main conversion steps from (wet) agricultural biomass to SNG are the fermentation itself, raw-biogas upgrading including $CO_2$ and water removal and final grid injection (see Figure 4). However, biogas production and with that, biogas fermentation technology goes way back to around 1910 and Karl Imhoff.[14] The economic breakthrough in Germany only came around the year 2000, when the Renewable Energy Act (EEG) regulated the feed-in and compensation of electricity from renewables. The first combined upgrading plant for

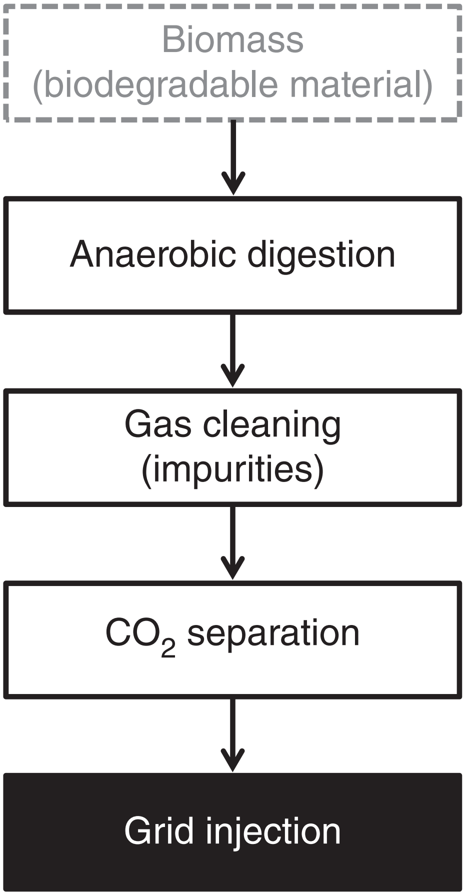

**FIGURE 4** | Simplified process scheme for biochemical SNG production.

SNG production was built in Germany on a biogas site in Pliening/Bavaria in 2006, where 920 $Nm^3/h$ biogas were purified by pressure swing adsorption (PSA) to 485 $Nm^3/h$ SNG with NG quality.[15,16] Today there are more than 120 upgrading plants installed in Germany (Europe: 180, status 2012) with a capacity of more than 71,000 $m^3/h_{i,N}$ SNG.[17] Worldwide, 277 biogas upgrading plants exist today with Germany and Sweden topping the list according to IEA Bioenergy Task 37.[18] An overview of the main process steps mentioned above is given in the following.

## Anaerobic Digestion

Production of the raw-biogas from biogenic feedstock is based on the anaerobic digestion of biodegradable materials such as manure, sewage, municipal waste, plant material, and energy crops. In the decomposition process, microorganisms (including acetic acid-forming bacteria and methane-forming archaea) transform organic matter under oxygen-free atmosphere into biogas and a solid residue. The process includes the four key biological and chemical stages of anaerobic digestion: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In the hydrolysis step the large organic polymers such as carbohydrates, proteins, and fats are broken down into smaller parts (monomers) such as sugars, amino acids, and fatty acids to enable better access by the bacteria. In the acidogenesis step, these monomers are broken down further by acidogenic bacteria into carbonic acids, alcohols, $H_2$, $CO_2$, and ammonia. During acetogenesis the molecules are further digested to produce mainly acetic acid and further $CO_2$ and $H_2$. The last step is methanogenesis, where methanogens use the small molecules and convert them into methane, $CO_2$, and water. Many factors influence these biological processes like pH-value, temperature, hydraulic retention time, substrates, carbon/nitrogen ratio, organic matter content, and many more. Product gas compositions vary greatly due to the broad range of feedstock. Table 2 shows typical biogas composition ranges.

A simplified overall expression of anaerobic digestion can be expressed as:

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4.$$

Digesters can be designed in different configurations like batch or continuous, mesophilic, or thermophilic, with high or low solid contents and in single- or multi-stage design. Configurations differ depending on the main design focus of the plant as either a waste treatment technology, which enhances environmental quality, or a sustainable energy producing technology. However, most biogas plants use mesophilic conditions and at least two vessels to optimize output and control.[14]

## Gas Cleaning (impurities)

In most cases, a first step in the cleaning of raw-biogas is the condensation of water, preventing downstream equipment like pumps, pipes and further cleaning devices from contact with corrosive condensate. Cyclone separators, water or moisture traps and demisters can be used for the physical separation of water down to a dew point of approximately 1°C. Chemical drying methods like adsorption of water vapor on silica, activated carbon, aluminum or magnesium oxide (adsorption dryer) as well as absorption of water in triethylene glycol are used for fine removal to typically permitted water contents of 100 $mg/m^3$ or dew points of −20°C, respectively. All chemical drying methods require regeneration.[21]

**TABLE 2** | Typical Biogas Composition with Characteristics (data from Refs 19,20)

| Component | Range of Concentration | Average Concentration | Characteristics |
|---|---|---|---|
| $CH_4$ | 45–75% | 60% | - Flammable component |
| $CO_2$ | 25–55% | 35% | - Diminishes calorific value and ignition behavior<br>- Enhances corrosion<br>- Detrimental influence on alkaline fuel cells (AFC) |
| $N_2$ | 0.01–5% | 1% | - Diminishes calorific value and ignition behavior |
| $O_2$ | 0.01–2% | 0.3% | - Explosive mixture with methane |
| $H_2S$ | 10–30,000 mg/m$^3$ | 500 mg/m$^3$ | - Corrosion in aggregates and pipelines<br>- $SO_2$-emissions after combustion<br>- Catalyst poison |
| Organic sulfur | <0.1–30 mg/m$^3$ | <0.1 mg/m$^3$ | - $SO_2$-emissions after combustion |
| $NH_3$ | 0.01–2.5 mg/m$^3$ | 0.7 mg/m$^3$ | - Diminishes ignition behavior<br>- Detrimental influence on fuel cells<br>- $NO_x$-emissions after combustion |
| BTX | <0.1–5 mg/m$^3$ | <0.1 mg/m$^3$ | - Carcinogenic |
| Siloxane | <0.1–5 mg/m$^3$ | <0.1 mg/m$^3$ | - Silicon dioxide after combustion–> mechanical corrosion in engines |
| Water (at 25°C/1.013 mbar) | 100% humidity | 100% humidity | - Corrosion in aggregates and pipelines<br>- Condensate spoils measuring instruments and aggregates<br>- Icing in pipelines and nozzles |
| Dust | >5 µm | n/a | - Obstruction of nozzles |

There are two options for the removal of $H_2S$ from the raw-biogas: *in situ* removal of $H_2S$ within the digester and downstream removal after the digester. Within the digester, $H_2S$ can be reduced by aerobic oxidation of $H_2S$ to elemental sulfur with the help of specialized microorganisms. Iron chloride can also be added to the digester to form FeS particles which can be removed from the system. However, both *in situ* systems do not normally reach the required reduction levels of $H_2S$ and may also cause some problems with regard to process control (difficult dosing). For fine removal of $H_2S$ downstream of the digester, various other measures can be applied: adsorption using iron oxide or hydroxide, absorption in liquids like water or a diluted NaOH-solution as well as a $FeCl_2$- or $Fe(OH)_3$-solution. Furthermore membrane separation (e.g., by a microporous hydrophilic membrane), biological filtration (similar to the *in situ* oxidation by microorganisms) or adsorption on activated carbon may be applied.[21]

Removal of other trace components like siloxanes, halogenated carbon hydrates, oxygen/air, and $NH_3$ may only be of interest in some specific cases, especially when the gas comes from landfills or municipal waste biogas plants. These components are often simply removed together in some activated carbon guard bed or are reduced in the $CO_2$ separation step. Siloxanes cause severe damage in engines during combustion by depositions of crystalline silicon oxide on the inner surfaces and moving parts. Maximum permitted levels vary in the range of 0.03–28 mg/m$^3$.[21] Removal may be done either by absorption in organic solvents or strong acids, but more commonly by adsorption on silica gel and activated carbon. Halogenated carbon hydrates and $NH_3$ are also present mainly in landfill gas and removed by activated carbon.

## $CO_2$ Separation

By $CO_2$ removal, the calorific value of the biogas increases while the relative density decreases leading to a higher Wobbe index of the product gas. Typical end specification for SNG from biogas is a value between 1 and 3% $CO_2$ in the gas. Several techniques can be used for $CO_2$ separation: physical and chemical absorption, pressure or vacuum swing adsorption (PSA/VSA) membrane separation and cryogenic separation. The most common treatment methods are pressurized water scrubbing (PWS, 41%), chemical scrubbing (22%) and PSA (21%).[18]

Pressurized water scrubbing uses water at elevated pressures (10–20 bar) as an absorbent in a packed, gas–liquid counter-flow column. The $CH_4$-rich, upgraded biogas leaves the column at the top stripped of $CO_2$ and also $H_2S$, whereas the laden water has to be stripped of the dissolved gas components also containing $CH_4$ in small amounts and recycled to the process. At atmospheric pressure, $CO_2$ and $H_2S$ are stripped in the desorption column with air or steam and released to the environment. Owing to the difference in solubility of $CO_2$ and $CH_4$, separation efficiencies above 97% and $CH_4$ losses below 2% are achieved.[21] Instead of water, polyethylene glycol (Selexol™), or amines (MEA, DEA, and MDEA) can also be used as sorbents. These washes are state-of-the-art in large-scale industrial processes with the advantage of better solubility compared to water, and a low vapor pressure of the sorbent which minimizes losses of chemicals (Figure 5 shows a simplified process flowsheet for an amine scrubbing unit). Separation efficiencies up to 99% and methane losses of less than 0.1% can be achieved.[21]

PSA/VSA use alternating batch process adsorption on molecular sieves like silica gel, zeolites or in most cases activated carbon for $CO_2$ (and $H_2O$) removal. The adsorption on the surface of the adsorbent material is reversible though, which enables subsequent desorption at a lower pressure level (regeneration). Since $H_2S$ also binds irreversibly to the molecular sieve, which requires dry gas, impurities have to be removed beforehand. PSA plants can be run under equilibrium or kinetic conditions (depending on residence times) while selectivity is mainly adjusted by mesh size and different operating pressures. Usually at least four pressure vessels are used to maintain continuous operation since one vessel always has to be regenerated while the others are in the process of pressurization and depressurisation. Intelligent process adaption and recirculation of feed gas, increasing the number of phases and the number of columns leads to high efficiencies (<99%) and low methane losses (<1.5%), but economics determine the most suitable configuration according to the scale of the plant.[22]

Membranes are dense filters which are able to separate substances on a molecular level based on selective permeability. Thus the gas stream is split into two parts, a permeate fraction (molecules with high permeability that pass through the membrane like $CO_2$ and $H_2S$) and a retentate fraction (molecules with low permeability that stay in the main gas stream like $CH_4$). Figure 6 shows the relative permeation rate of molecules. Favoring small-scale applications (<300 $Nm^3/h$), operation pressures are usually up to approximately 36 bar with maximum $CH_4$ yields up to 92% for single-stage systems, whereas multi-stage systems can achieve results in excess of 96%.[21]

Membranes can be made of polymers like silicone rubber or cellulose acetate as well as polyimide or even liquid membranes. Most commercial systems

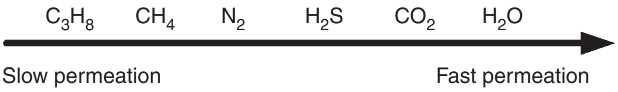

**FIGURE 6** | Relative permeation rate of biogas molecules.

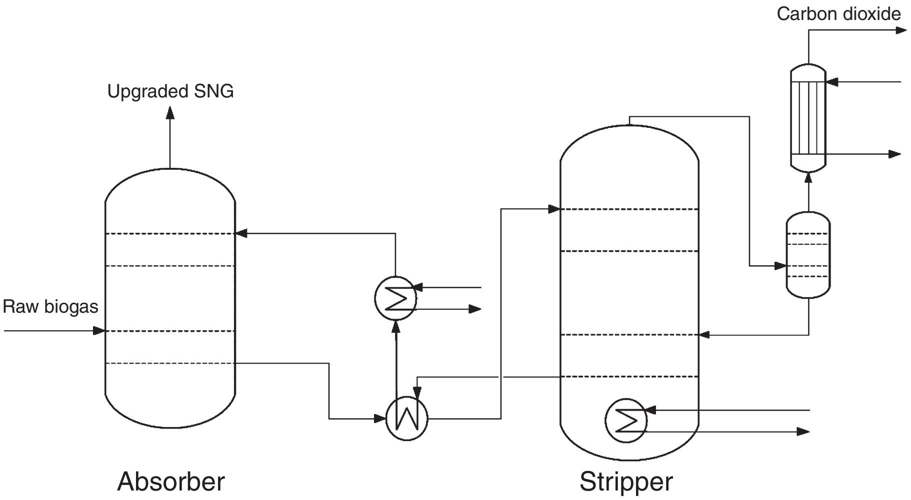

**FIGURE 5** | Simplified amine scrubbing process flowsheet (adapted from Ref 22).

use hollow fibers;[23] however, membrane technology is in an early stage of development with a growing number of applications. Gas–liquid membranes using amines or aqueous solutions for example have only been developed recently. Also combinations of membrane systems with PSA units are investigated as well as new materials for enhanced selectivity, better resistance toward undesired gas components and cost optimization.[23]

Cryogenic separation based on the different liquefaction temperatures of gas components can also be used for $CO_2$ separation. However, with necessary temperatures of down to −85°C and pressures in the range of 80 bar, the technology is very energy intensive.

In the end, the decision for a specific cleaning technology is influenced by many factors including the proximity to excess heat, the abundance of local suppliers, efficiencies, the costs of utilities (power, water, chemicals, etc.), investment, and many more.

### Grid Injection

For grid injection, the following components have to be considered: connecting pipe, compressors, optional storage tanks, pressure control and measurement equipment, gas composition measurement, odorant addition system and conditioning and gas mixture facility. Most important, the raw-SNG is pressurized above grid level mainly by redundant piston or turbo compressors, whereas the pressure levels vary due to injection location and the local grid (high-pressure transmission or low pressure distribution network, usually in the range of 0.1–16 bar). Volume flow and Wobbe index are controlled and adjusted if necessary by the addition of liquefied petroleum gas, mainly propane, and an odorant is added to the gas to fulfill injection requirements.[17]

## THERMOCHEMICAL SNG PRODUCTION

Thermochemical SNG production from dry, lignocellulosic biomass is a more recent concept not yet fully applied on an industrial scale with only a few and small-scale test and pilot plants in operation.[24–28] Thus there is no operation data available yet for long-term experience on an industrial scale.

Dry, lignocellulosic biomass is converted in a gasification and gas treatment process to supply the feedstock for higher, universally applicable valorization. The main process steps are fuel pretreatment, gasification, gas cleaning, and methanation followed by the final gas upgrading steps and grid injection (see Figure 7).[29]

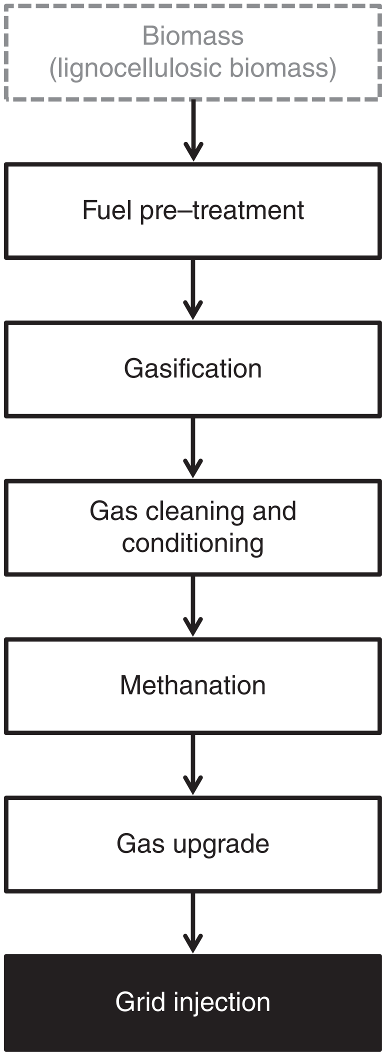

**FIGURE 7** | Simplified process scheme for thermochemical SNG production.

### Fuel Pretreatment

The first step in the process is the optional biomass pretreatment step. Depending mainly on the water content and the subsequent gasification technology, the raw material has to be prepared for gasification. Drying, grinding, pelletizing, homogenisation, sieving and screening, separation, etc. may have to be carried out to ensure appropriate input specifications for the gasification. For entrained flow gasification (EFG) in particular, an intensive sizing of the biomass below 0.1 mm is necessary to ensure high fuel conversion.[30] To reduce the energy demand of grinding biomass pretreatment like torrefaction or hydrothermal carbonization (HTC) is investigated.

## Gasification

By gasification, solid biomass is converted into a gaseous energy carrier. Typically the gasification process can be described using the following simplified reaction (adopted from Ref 31):

$$\text{Biomass} \rightarrow \text{char} + \text{tars} + CO + CO_2 + H_2 + H_2O + CH_4 + (C_2 - C_5) + \text{impurities}. \quad (1)$$

Gasifiers can be classified by the type of reactor (fixed bed, fluidized bed, and entrained flow), the energy supply (allothermal or autothermal) the gasification agent (air, oxygen, steam, or carbon dioxide) or by the working pressure in the reactor (pressurized or atmospheric).[32] Figure 8 shows the different reactor types.

For subsequent SNG production, allothermal gasification with an external heat supply (e.g., through separated combustion chamber) or autothermal gasification with oxygen is favored to prevent nitrogen dilution of the product gas. Therefore indirect steam-blown fluidized bed and pressurized oxygen-blown EFG as described briefly in the following are most suitable:

*Fluidized bed gasification* (FBG) is a well-known technology and state-of-the-art in small- to medium-scale biomass applications. However, there is a broad variety of gasifier concepts available which differ greatly in terms of process engineering (e.g., stationary, circulating or multi-bed configurations) and process parameters (gasification temperature and pressure, fluidisation medium, etc.). Prominent concepts are the MILENA gasifier (Netherlands), the FICFB (Fast Internally Circulating Fluidized Bed) gasifier in Güssing (Austria), and the Värnamo gasifier (Sweden).[27,28] The gasification temperature is limited to 700–1000°C by the ash softening point due to agglomeration of the bed material. The moderate temperature results in high tar contents requiring intensive gas cleaning or *in situ* tar reduction measures.[34] Current pilot plants are operated at pressures up to 20 bar. A review of most recent state-of-the-art technologies is given in Ref 35.

EFG is a well-researched and -developed technology in coal gasification but still lacks research and application in biomass gasification. In 2010, 82 out of 87 registered gasification projects worldwide (in operation and planned) were based on EFG mainly using coal and pet coke as feedstock.[34] EFG usually operates at elevated pressures of up to 60 bar and high temperatures of 1100–1400°C resulting in a high-quality, tar-free product gas. The transformation and adaption of the technology toward biomass leaves various challenges like fuel pretreatment, oxygen supply and ash properties to be solved.[30]

*Fixed bed gasification* is a proven technology for coal gasification on an industrial scale (e.g., Lurgi gasifiers) and for biomass gasification in medium- (e.g., Nexterra[36]) to small-scale applications (e.g., Xylogas,[37] Burkhardt,[38] Spanner[39]). Especially when it comes to oxygen-blown biomass gasification in fixed bed, a constant and uniform fuel supply (quality, wetness, particle size and form, composition, etc.) is crucial due to regulation and constant gas output requirements.

Table 3 gives an overview of relevant gasifier product gas compositions (main components).

## Gas Cleaning and Conditioning

Depending on the gasification technology applied, different levels and types of contaminants are present

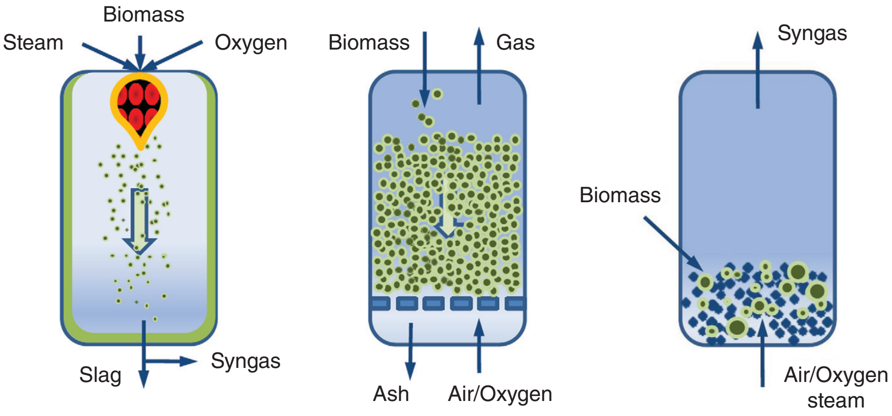

**FIGURE 8** | Gasifier types. Entrained flow (left), fixed bed (middle), and fluidized bed (right) gasifier.[33]

**TABLE 3** | Typical Compositions of Product Gases from Different Gasifiers in % (permanent gases only)[33]

| Gasifier | Heating | Oxidant | $H_2$ | CO | $CO_2$ | $H_2O$ | $CH_4$ | $N_2$ |
|---|---|---|---|---|---|---|---|---|
| REPOTEC (CFB) | Indirect | Steam | 38–45 | 22–25 | 20–23 | | 9–12 | 2–3% |
| CUTEC (CFB) | Direct | $O_2$/steam | 31.6 | 22.0 | 33.6 | | 7.9 | |
| MILENA (CFB) | Indirect | Steam | 18.0 | 44.0 | 11.0 | 25.0 | 15.0 | 4.0% |
| CHOREN (EF) | Direct | $O_2$ | 37.2 | 36.4 | 18.9 | 7.3 | 0.06 | 0.1% |
| KIT (EF) | Direct | $O_2$ | 23 | 43 | 11 | | <0.1 | 5% |

**TABLE 4** | Typical Contaminants Present in Biomass Gasification Synthesis Gas[40]

| Contaminant | Range | |
|---|---|---|
| Tars | 2–20 | g/Nm$^3$ |
| Particles | 10–100 | g/Nm$^3$ |
| Alkali metals | 0.5–5 | ppm |
| $H_2S$ | 50–100 | ppm |
| COS | 2–10 | ppm |
| $NH_3$ | 200–2000 | ppm |
| Halogens | 0–300 | ppm |

in the product gas of the gasifier. The most relevant pollutants for gas cleaning considering SNG production are: particulate matter (ash and bed material), tars and higher hydrocarbons, sulfur ($H_2S$, COS, thiophenes, etc.) and nitrogen ($NH_3$) compounds, halogens (mainly HCl), as well as alkali metals. Typical ranges for contaminants in biomass gasification plants are shown in Table 4.

Gas cleaning methods can be divided into hot gas cleaning (HGC) and cold gas cleaning (CGC), according to the temperature ranges applied—mainly below 80°C or up to 1000°C, respectively. Technologies for the removal of these contaminants are described in the following.

*Cold gas cleaning* is mainly based on liquid scrubbing technologies, removing a couple of contaminants from the process gas in one step with high process maturity in industrial scale as well as in small-scale units (down to the size of container-solutions). Wet electrostatic precipitators, wet scrubbers, and wet cyclones are used (e.g., RME scrubber, MEA/MDEA washes, etc.). Dry cold gas cleaning may consist of a combination of cyclones, fabric filters, adsorbers (e.g., activated carbon), and sand filters.[41] However, due to the low-temperature levels, significant cooling and subsequent reheating of the gas stream for downstream synthesis are required, lowering overall efficiencies, and increasing exergy losses, respectively.

Gas scrubbers operated at around 60–80°C (single- or multi-stage) can be applied for the removal of tars, particulate matter and other contaminants depending on the scrubbing liquid. Water and more often RME (rapeseed methyl ether) or biodiesel scrubbers are used with the advantage of simple thermal utilization of the loaded liquid in the combustion zone or chamber of the gasifier. Thus elaborate cleaning of the liquid is not necessary. Furthermore, the cooling and absorption step has the inherent advantage of removing a broad range of unwanted contaminants in the same step. Afterwards additional adsorptive measures can be taken for fine tuning to reach required contaminant levels. From a technology point of view, cost optimization and process integration especially the recycling of, e.g., the loaded scrubbing liquid are of main interest.[41,42]

Owing to easy handling and high maturity of the technologies, wet CGC processes have been used in the first thermochemical pilot and demonstration plants so far. To minimize technological risks, the efficiency losses are accepted and preferred over process safety and operating hours for example in Güssing (in combination with fluidized bed methanation unit) and in Gothenburg at the GoBiGas demonstration plant as well as in most operating projects today.[25,28]

*Hot gas cleaning* is designed for minimizing downstream maintenance and designed to increase efficiencies due to the exergetically more favorable temperature control without the need for rapid cooling down of the product gas with subsequent reheating for following process steps. With temperatures well above 200°C, many process configurations benefit thermochemically, e.g., by reduced waste streams and increased efficiencies. However, many hot gas cleaning steps are still under development with only a limited number of first industrial-scale applications. The single design specifications of a gas cleaning process suitable for the application on hand may vary greatly due to scale, operational approach, economics, and requirements; however, the following components may be part of the involved processes:

Cyclones are the most commonly used initial separation devices for raw-gases from gasification with up to 99.6% separation efficiency and removal limits down to the μm-range. Simplicity of design with no moving parts enables high-temperature application limited only by the mechanical strength of the material. Filtration in the form of barrier filters (e.g., granules, fibres, or porous monolithic structures) is often used downstream of a cyclone. Fabric or rigid filters (e.g., ceramic and metallic candle filters) as well as fixed and moving bed granular filters or sintered metal filters are applied in many cases, while the filtration effect can be enhanced by precoating of the particles (for example with CaO). Recent developments also focus on the incorporation of catalytic active materials into various filter constructions or the use of electrostatic precipitators (ESPs) at elevated temperatures.[42]

Alkali components have to be separated either by co-removal with other contaminants through condensation mechanisms (usual condensation range around 600–650°C) or with the help of better materials (e.g., natural minerals like bauxite or kaolinite). Tars can be removed (if no sufficient *in situ* removal was applied within the gasifier) by thermal or catalytic reforming/cracking. In contrast to the CGC option, the chemical energy content does not leave the system, resulting in efficiency advantages. Sulfur and chlorine components are removed in most cases by adsorption (in combination with an upstream hydro desulfurisation unit if necessary).[41,42]

Depending on the scale, the operation conditions and the feedstock of the process, there might be the need for a CO-shift (water gas shift reaction) upstream of the methanation to adjust the $H_2$/CO ratio (target for the $H_2$/CO ratio is a stoichiometric value of three). Equation (2) shows the water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0{}_R = -41\ kJ/mol. \quad (2)$$

However, the CO-shift also runs in *in situ*, parallel to methanation, which is why it is not regarded separately in this overview.

## Methanation

After gas cleaning, the methane content has to be increased to meet grid injection levels. This is achieved by the heterogeneous catalytic methanation process where carbon oxides are hydrogenated to methane. The exothermic reaction is usually catalyzed by commercial nickel catalysts, with possible alternative metals being: Ru, Rh, Pt, Fe, and Co.

CO- and $CO_2$-methanation reactions are given in Eqs (3) and (4):

$$3H_2CO + CO \rightarrow CH_4 + H_2O \qquad \Delta H^0{}_R = -206\ kJ/mol. \quad (3)$$

$$4H_2CO + CO_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H^0{}_R = -165\ kJ/mol. \quad (4)$$

$CO_2$-methanation reaction can also be described by linear combination of the CO-methanation (Eq. (3)) and the reverse water gas shift reaction (back reaction of Eq. (2)). In case of a stoichiometric value of three or more in the synthesis gas, only CO-methanation (Eq. (3)) will occur, but under normal circumstances there is a lack of hydrogen in the synthesis gas and $H_2$/CO ratios are between 0.3 and 2. Thus part of the CO is converted by Eq. (2) to $CO_2$ and additional $H_2$.

Furthermore, the Boudouard reaction (Eq. (5)) is important for methanation since carbon depositions are crucial during methanation in two ways: carbon depositions in the form of gum (polymeric carbon) and whisker formation cause catalyst deactivation by blocking of the surface and by encapsulation of Ni crystallites respectively. However, carbon also is a necessary intermediate on the catalyst surface during hydrogenation.[43]

$$2CO \rightarrow C + CO_2 \qquad \Delta H^0{}_R = -173\ kJ/mol. \quad (5)$$

As all reactions are exothermic, heat removal is of great importance, influencing thermodynamics, reaction mechanisms, and kinetics. For high methane yields, low temperatures, and high pressures are favored due to the law of le Chatelier. Deactivation and poisoning of the catalyst (especially Ni catalysts) with regard to, e.g., sulfur species ($H_2S$, COS, thiophenes, organic sulfur) and chlorine components as well as other aging and degradation processes have to be considered.

Methanation technology can be classified by different approaches of the catalyst and technology suppliers. Operating and planned processes use at least two reactors in most cases with recycling of part of the product gas and with intercooling after or direct cooling inside the reactors. However, two fundamentally different approaches are possible: either enhancement of efficiency through high-temperature process heat utilization (via high-pressure steam production) requiring enhanced temperature stability of the catalyst and intercooling between sequential adiabatic reactors, or temperature limitation through dilution of feed gas with recycled gas and/or polytropic reactors with direct internal cooling (e.g., isothermal Linde reactor). Main issue and determining factor in each case is the development of the appropriate Ni-catalyst with the required thermal stability and performance as well as design of the heat removal. Methanation process technologies date back to the 1960s and '70s and can be separated according to the applied reactor types: fixed bed methanation, fluidized bed methanation, liquid-phase methanation (or three-phase methanation). Favoring fixed bed methanation, the Lurgi methanation process (Figure 9) and the TREMP process developed by Haldor Topsøe are the most relevant and prominent examples for fixed bed methanation processes. Fluidized bed methanation research was carried out, e.g., by the Bureau of Mines (US), BCR (Bituminous Coal Research Inc., US), and Thyssengas GmbH (Germany) leading to the different fluidized bed reactor concepts with the COMFLUX process (by Thyssengas, University of Karlsruhe and Didier Engineering GmbH) as one of the more well-known processes. Liquid-phase methanation was proposed by ChemSystem Inc. (US) as a promising process due to enhanced temperature control and easy removal of process heat, but the development activities were terminated after a few years.[43]

The Bio-TREMP methanation technology by Haldor Topsøe (Figure 10) is the only applied technology in combination with biomass gasification ('Güssing'-type dual fluidized bed gasifier supplied by Repotec), dealing with the specific problems caused by biomass feedstock such as organic sulfur impurities and smaller scale.

However, there are various other research institutes and companies working on different methanation technologies and reactor designs in varying stages of development (see Refs 29,31,43).

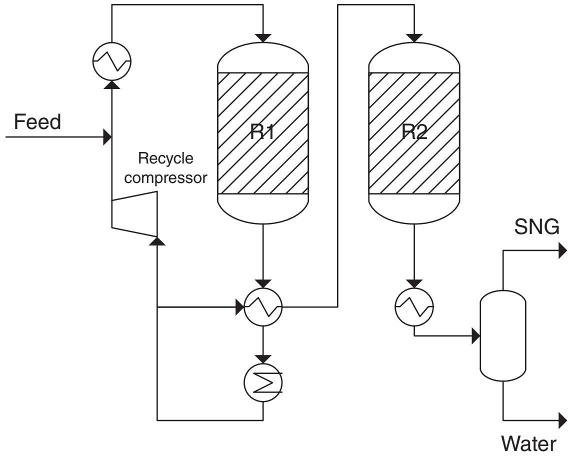

**FIGURE 9** | Lurgi methanation process flowsheet (adapted from Ref 43).

## Gas Upgrade and Grid Injection

After methanation water vapor has to be separated from the product gas which is usually done by condensation and cooling down of the raw-SNG from the methanation unit. Furthermore, surplus $CO_2$ and if required also $H_2$ have to be separated from the product gas stream. Technologies for final gas upgrade can vary due to product gas specifications after methanation. Membrane technology, scrubbing systems or adsorption technologies (e.g., PSA) may be applied (see Biochemical section). Last step in the process is the grid injection and the required legal control systems. With no industrial application so far, exact layout of the necessary measures will most likely be similar to those applied for biochemical SNG injection.

# ELECTROCHEMICAL SNG PRODUCTION

Beside the biomass-based options, the electrochemical generation of hydrogen using water electrolysis offers the possibility of also using wind and solar energy as feedstock for renewable SNG production. The carbon source in this case is carbon dioxide. In recent years, the concept has become popular as a possible long-term energy storage option, balancing demand and fluctuating supply of wind and solar in a future renewable energy system. A simplified scheme of the electrochemical SNG production route also known as Power-to-Gas concept (PtG) is shown in Figure 11.

Electrical energy from renewable energy sources like wind and solar is converted via water electrolysis to hydrogen. In a subsequent step, $H_2$ and $CO_2$ are converted to $CH_4$. The SNG can be fed into the NG grid after a final gas upgrade which is mainly water removal by condensation and surplus $H_2$ removal by membrane. The required $CO_2$ can be sequestrated from several $CO_2$-neutral sources like biogas production, biomass gasification, waste incineration, or recycling from fossil power plants. In addition, the utilization of $CO_2$ from the air has been tested.[45] Owing to the utilization of $CO_2$, this technology can be regarded as alternative to the intensively discussed carbon capture and sequestration (CCS) technology efficiently using the $CO_2$ instead of sequestrating it. $CO_2$ and $H_2$ buffer storages allow a decoupling of the electrolyser as well as $CO_2$ sequestration from the methanation process. The additional conversion step from $H_2$ to SNG offers the advantages of threefold higher energy density and an unlimited utilization of the existing NG infrastructure through feed-in

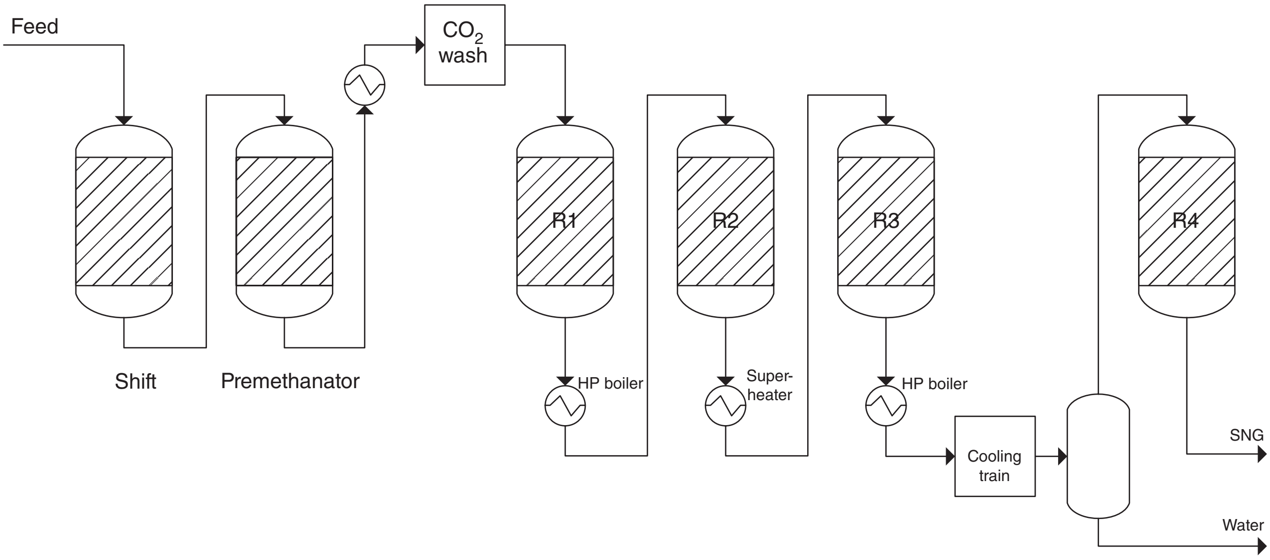

**FIGURE 10** | Typical process flowsheet of the Bio-TREMP process by Haldor Topsøe (adapted from Ref 44).

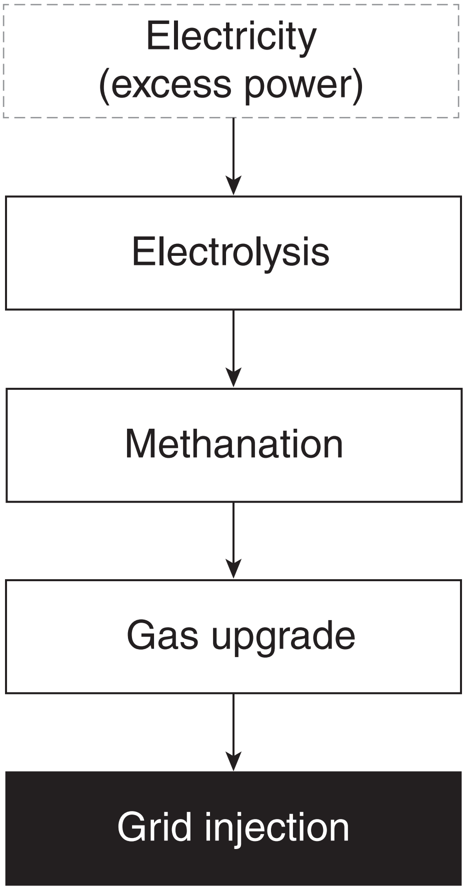

**FIGURE 11** | Simplified process scheme for electrochemical SNG production.

of the SNG. While the key processes of the electrochemical SNG production are well established, the dynamic operation and interaction between the processes represent a major technical challenge.

### Electrolysis

Available processes for the electrochemical decomposition of water into $O_2$ and $H_2$ are alkaline electrolysis (AEL) with a concentrated aqueous solution of KOH (25–30 wt%) as electrolyte, proton exchange membrane electrolysis (PEMEL) with a polymer electrolyte and high-temperature electrolysis (HTEL) with a solid oxide electrolyte (also known as solid oxide electrolysis).

In contrast to the HTEL operation temperature of 700–1000°C, AEL and PEMEL are operated at temperatures below 100°C. While alkaline and PEM electrolysis are state-of-the-art technologies (Table 5), HTEL is still in the fundamental research state with lab-scale systems in the kW-range, suffering from high degradation rates to the order of 3–5%/1000 h.[49] AEL is the most mature electrolysis technology with several industrial-scale plants constructed especially in the mid of the 20th century. Examples are the plants located in Aswan (Egypt) with a capacity of 32,400 Nm$^3$/h (160 MW) installed by DEMAG in 1939, in Nangal (India) with a capacity of 30,000 Nm$^3$/h (142 MW) installed by DeNora in 1961 or in Rjukan (Norway) with a capacity of 27,000 Nm$^3$/h (142 MW) commissioned in 1929 (decommissioned in 1971) manufactured by Norsk

**TABLE 5** | Comparison of Commercial Electrolysis Technologies[46–48]

| Name | Alkaline | PEM |
|---|---|---|
| **Operation parameters** | | |
| T [°C] | 40–90 | 20–100 |
| Max. pressure [bar] | 30 | 85 |
| Current density [A/cm$^2$] | 0.2–0.4 | 0.5–2 |
| Min. part-load [%] | 15–25 | 0 |
| **State of the art** | | |
| Efficiency [%] (HHV) | 63–84 | 60–84 |
| (LHV) | 53–71 | 51–71 |
| Max. module power [MW] | 3.5 | 0.75 |
| Investment costs [€/kW] | 700–1100 | 1300–2200 |

Hydro.[46,50] These plants are used for the production of ammonia in regions with low-priced electric energy resulting from large hydro power plants in combination with an underdeveloped electric grid. Large production capacities are realized by parallel arrangement of several electrolyser modules. Alkaline electrolysers are available on a module level with very high $H_2$ production capacities of up to 760 Nm$^3$/h corresponding to an electric power consumption of about 3.5 MW.[47] In contrast, PEM electrolysis modules are just about to be scaled-up, mainly driven by the PtG market potential. Currently they are available on a module level with capacities up to 10–15 Nm$^3$/h.[51–53] Combining several modules, system capacities in the MW-range are realized, such as the 1 MW PEM system of EON in Hamburg to be commissioned by 2014.[54]

The main advantage of PEM electrolysis for PtG applications is its superior dynamic behavior. While AEL is limited to a minimal part-load in the range of 15–25% of nominal load, PEM can be operated from 0 to 100% (some manufacturers claim that overload is also possible, but this is more a case of definition of the nominal operation point).[46,47] The minimal load limitation of AEL is given by diffusion of product gases across the diaphragm resulting in a flammable mixture.[55] For PEMEL systems very fast load change rates of 0–100% in 1–10 s are reported.[56,57] AEL also offers high flexibility with load change rates in the range of 50–100%/min.[58–60]

As electrolyser efficiency increases in part load, the performance is best characterized by the voltage–current density curve. Here, specific electrical energy consumption is directly proportional to the voltage, and the specific $H_2$-production per cell area is directly proportional to the current density. Exemplary characteristic U–j curves of AEL, PEMEL, and HTEL are presented in Figure 12.

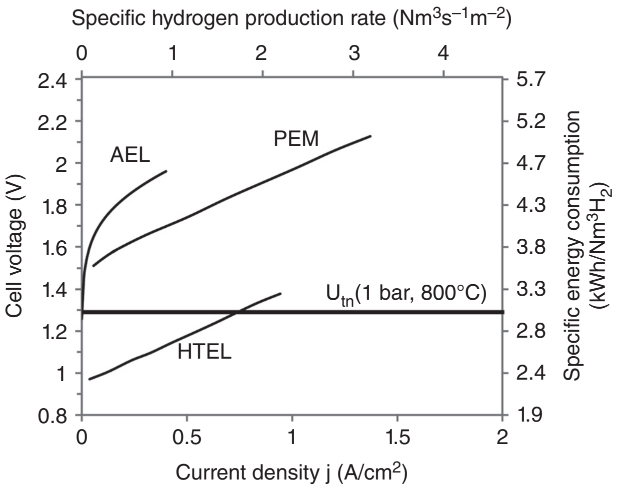

**FIGURE 12** | Exemplary experimental characteristic U-j-curves for AEL (Casale Chemicals, 25 kW, 20 bar, 70°C[61]), PEMEL (Giner, 5.6 kW, 7 bar, 58°C[62]) and HTEL (single cell test, 1 bar, 750°C[63]).

Decreasing the load corresponding to a lower current density results in a lower voltage or decreased specific energy consumption, respectively. The main potential of HTEL lies in the reduced electrical energy consumption compared to the low-temperature processes. This results from faster reaction kinetics and lower internal resistance at higher temperatures as well as low temperature heat integration for water vaporization. Usually HTEL is operated at thermoneutral voltage where the heat produced in the cell and the heat consumed by the electrolysis reaction is equal, resulting in a constant cell temperature. In contrast to this, AEL and PEMEL are operated above thermoneutral voltage at nominal load, requiring active cooling of the cell. The highest current densities are achieved by the PEMEL technology with 0.5–2 A/cm$^2$ compared to AEL with 0.2–0.4 A/cm$^2$.[46] This also implies a reduced cell area required for PEMEL. Despite this, specific costs of PEMEL amounting to 1300–2200 €/kW are still higher than for AEL at 700–1100 €/kW.[48] This difference mainly results from the more expensive membranes and noble metal based electrodes. At nominal load, the electrolyser efficiency, defined as the higher heating value (HHV) of the produced $H_2$ divided by the power input, lies in the range of 60–84% (0.5–2.0 A/cm$^2$) for PEM and 63–84% (0.2–0.4 A/cm$^2$) for AEL.[46] PEM is more suitable for pressurized operation due to the compact design. Nevertheless, PEM as well as AEL are commercially available for high-pressure operation. Therefore the more efficient compression of liquid water can replace the subsequent effort for compression of the product gas.

## $CO_2$-methanation

Methanation of $CO_2$ and $H_2$ basically applies the same processes as described before in the synthesis gas methanation section. The main differences are a lower reactivity of the $CO_2$-methanation reaction compared to CO-methanation and a reduced production of reaction heat, facilitating reactor cooling (see Eqs (3) and (4)). In multi-stage fixed bed processes experience of $CO_2$ methanation has already been gained from the conversion of synthesis gases. While the complete CO is converted in the first stages, $CO_2$ conversion takes place in the last stages in absence of CO.[64,65] Experiments focusing on $CO_2$-methanation were conducted in pilot-scale and lab-scale plants by the Centre for Solar Energy and Hydrogen Research (ZSW) for fixed bed methanation[60,66] and by the Engler-Bunte-Institute for three-phase methanation.[9]

In addition, dynamic operation of methanation reactors is being investigated. In an early project concerning nuclear district heating consisting of a steam reformer and a methanation unit (10 MW), the methanation unit was operated flexibly between 30 and 100%.[67] Start-up time was determined by the PSI within the research conducted at the 1 MW fluidized bed methanation unit in Güssing to be around 30 min.[68] An example of load changes and start/stop operation is presented in Figure 13 for a 250 kW fixed bed plant showing the fast start-up within about 5 min when the reactor is held at ignition temperature. Furthermore, a catalyst stability of 900 cycles was proven. The gas quality achieved was 92% $CH_4$ (3.3% $H_2$, 3.8% $CO_2$) without gas purification and 98.7% $CH_4$ (0.5% $H_2$, 0.8% $CO_2$) with subsequent gas upgrade by membrane separation ($\Delta p_{\text{membrane unit}} = 5$ bar).[60]

## Gas Upgrade and Grid Injection

Analog to the other options, final gas upgrade is needed to reach grid specifications. Assuming dynamic SNG production, measures for gas upgrade and grid injection have to be adjusted to that. Thus, e.g., membrane cleaning technology might be more suitable for fluctuating feed but buffer storage solutions could also diminish the fluctuations.

## ALTERNATIVE/HYBRID CONCEPTS

Besides the stand-alone concepts described above, combined or hybrid systems are investigated and applied in different combinations.

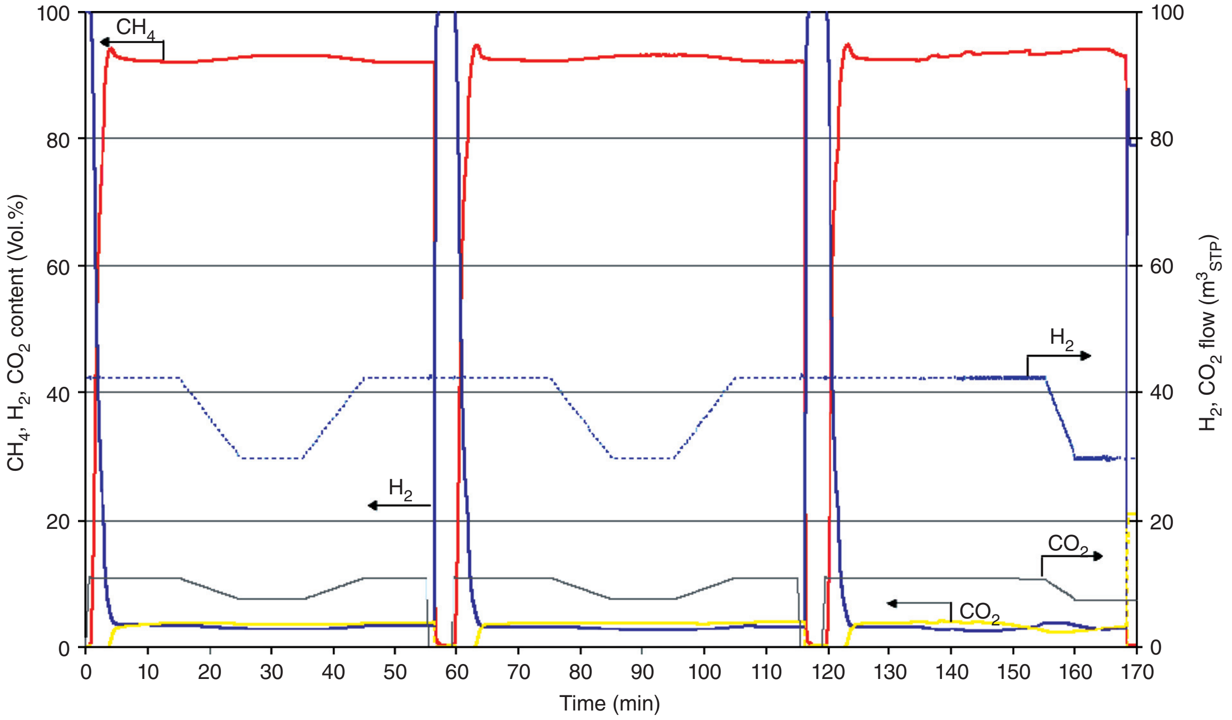

**FIGURE 13** | Dynamic operation of 250 kW methanation unit.[60]

## Biochemical Pathway with Excess Power Integration

For example, the electrochemical SNG production pathway is usually combined with a biochemical SNG production. Therefore the separated $CO_2$ from the biogas upgrading unit can be utilized as educt gas for the methanation unit with $H_2$ from the electrolysis unit. This has a great synergy effect in that it uses the $CO_2$ which is normally blown into the atmosphere as a valuable, clean educt for the second process. Heat from the methanation can in return be used for the initial $CO_2$ separation (e.g., in the form of heat for the stripper column to regenerate the amine wash). This combination of biogas upgrading plants and electrolysis unit is used in most operating and planned PtG plants.

It is also proposed to combine the two processes in such a way that $H_2$ from electrolysis is directly injected into the digester (or a second digester/fermenter) to hydrogenate the remaining $CO_2$ *in situ* in the biogas, thus saving the subsequent separation unit. However, this direct methanation concept is still at the research stage, with problems such as the distribution and solution of $H_2$ in the fermenter still to be solved.[69]

## Thermochemical Pathway with Excess Power Integration

The combination of thermochemical SNG production with excess power integration (electrochemical SNG production) also has some advantages. Here both, the $H_2$ (e.g., in the methanation unit) as well as the $O_2$ from the electrolysis unit (e.g., as replacement for the air separation unit or to enable catalytic tar cracking via partial oxidation) can be used in a very efficient way within the thermochemical SNG production process.

Process simulations have shown that in small-scale applications, the integration of an electrolysis unit into the process can have efficiency synergies due to heat integration and reduced complexity of both processes. It has been shown that the integration of electrolysis units into the thermochemical route can enhance methane yields up to nearly 98%, meaning almost full conversion of the biogenic carbon into methane and almost no losses of carbon or $CO_2$ respectively to the environment. Furthermore, cold gas efficiencies can be increased up to 73.8%.[70]

Other investigations show, that the storage efficiency of the combined concept can be improved by 3–4%-points compared to stand-alone PtG and biomass gasification concepts.[71]

# DISCUSSION AND COMPARISON OF CONCEPTS

## Market Maturity and Status Quo of Technological Development

The status quo of the different concepts varies significantly regarding market maturity levels and geographical extension as well as historical background. To measure and evaluate evolving technologies, Technology Readiness Levels (TRLs) have been introduced (see Table 6).

While biogas plants all over Europe started to increase from the 1990s, encouraged by government incentives, the upgrading of biogas to SNG only reached broad interest within the last 10–15 years. However, upgrading technologies, mainly $CO_2$ separation, have also proven maturity in small-scale applications over the last years with a capacity of more than 94,000 $Nm^3/h_{SNG}$ in Europe in 2012.[72] Thus biochemical SNG production can be seen at the highest TRL 9. All components are commercially available from a range of suppliers. However, besides high TRLs, there is research ongoing for example in the area of alternative and problematic feedstock like sewage sludge as well as gas cleaning and upgrading of landfill gas facilities.

Technical potential of feedstock for biogas utilization is more limited in comparison to lignocellulosic biomass, and in the worst case the cultivation of

**TABLE 6** | Definition of TRLs (Technology Readiness Levels) by the European Commission[18]

| | |
|---|---|
| TRL 0 | Idea. Unproven concept, no testing has been performed. |
| TRL 1 | Basic research. Principles postulated and observed but no experimental proof available. |
| TRL 2 | Technology formulation. Concept and application have been formulated. |
| TRL 3 | Applied research. First laboratory tests completed; proof of concept. |
| TRL 4 | Small-scale prototype built in a laboratory environment ('ugly' prototype). |
| TRL 5 | Large-scale prototype tested in intended environment. |
| TRL 6 | Prototype system tested in intended environment close to expected performance. |
| TRL 7 | Demonstration system operating in operational environment at pre-commercial scale. |
| TRL 8 | First of a kind commercial system. Manufacturing issues solved. |
| TRL 9 | Full commercial application, technology available for consumers. |

energy crops competes with other agricultural areas. Energy density in the first place determines the maximum scale of the plants which therefore should not increase in future.

As far as thermochemical SNG production is concerned, two trends can be identified globally: on the one hand, mainly China is increasing efforts to bring GW-scale Coal-to-SNG plants online to use the NG grid for energy transportation from the immense coal resources located mainly in remote areas to the urban centers for utilization.[73] In contrast to these TRL 9 type applications with a capacity of more than 2,000,000 $Nm^3/h$ in operation or under construction (calculated based on Refs 73,74), however, the analog biogenic pathway mainly followed by Europe in general and Scandinavia in particular still lacks full commercial implementation. Biomass gasification and especially most downstream process units adapted to biogenic syngas and scale-down are still in the research and technical demonstration phase. Thus the overall system can be incorporated at TRL 4–7. The recent lighthouse project is the GoBiGas project by Gothenborg Energy. In addition, various research institutes and companies are conducting research and development on the process. ECN (Energy Research Centre of the Netherlands) for example has developed a fixed bed methanation process in connection with the MILENA gasifier and OLGA gas cleaning technology. The ZSW in Germany is investigating the methanation of commercial Ni-catalysts downstream of an Adsorption Enhanced Reformer (AER) focusing on fixed bed methanation with molten-salt-cooled multi-zone reactors. The PSI (Paul Scherrer Institute) in Switzerland was one of the first to start investigating the thermochemical SNG production favoring fluidized bed methanation as core technology. Various research approaches are being carried out by TUM/IES, FAU/EVT, TUG, Agnion, KIT, GDF Suez, and many more. Today's major technological challenges include the commercial operation of the gasifier itself, tar reduction measures, deactivation and poisoning of the methanation catalysts by sulfur and carbon depositions (e.g., from ethylene), durability issues of various process steps, heat removal and utilization and many more.[24,43,68,75,76]

The electrochemical pathway is the newest concept, although the technological process steps involved such as electrolysis are already established in some other niche applications. The transformation toward large-scale, dynamic application in the energy system sector remains the challenge and hurdle to take in the meantime. The lighthouse project for electrochemical SNG production is the Power-to-Gas plant in Wertle, Germany, initiated by a consortium around the automotive company Audi. It consists of three atmospheric operated 2 MW alkaline electrolysers with a total $H_2$ production capacity of 1310 $Nm^3/h$ and a molten-salt-cooled fixed bed reactor for methanation of the $H_2$ and $CO_2$ from a nearby biogas plant.[77] The PtG technology in general is being highly supported in Germany in the course of the 'Energiewende' (exit from nuclear and fossil-fuel energy) and many similar projects and approaches are being bundled in a Power-to-Gas strategy platform.[78] TRL can be estimated to be in the range of 4–6.

As far as the technical potential is concerned, the amount of excess energy production due to a high energy generation of the fluctuating renewables in times of a low energy demand is very limited in the mid-term. This will become relevant only for a few countries with ambitious goals concerning the RE share or areas with a high amount of fluctuating renewable energy production and an underdeveloped electricity grid. For Germany, excess energy production in the range of 21.6–78.5 TWh/a is predicted for an RE share in the range of 75–100%.[6,8,79,80]

## Efficiencies

Comparing the conversion efficiencies of the three production pathways proves complex due to different feed streams. For the biochemical pathway, the feed consists mainly of energy crops (e.g., corn silage) and manure while for the thermochemical pathway dry wood is the main energy input. In contrast to this, the electrochemical pathway converts electric energy which has a higher value from an exergetic perspective compared to biomass. Beside this, the efficiency is dependent on various factors. These include system design, considered products like SNG, heat and power, system scale, injection pressure, and time horizon. Figure 14 displays the energy output referred to the total energy input which enables comparison of the energy utilization rate taking SNG, heat, power, biomass, and auxiliary substances like propane for gas conditioning and biodiesel for gas cleaning into account. The energy demand for allocation and transport of the biomass is not taken into account, although it becomes relevant in terms of limiting the maximum transport distance especially for raw materials with a low energy density.[87] In the following, efficiency is defined as products like SNG on LHV basis, electricity and heat divided by consumptions including biomass on LHV basis, electricity, and heat.

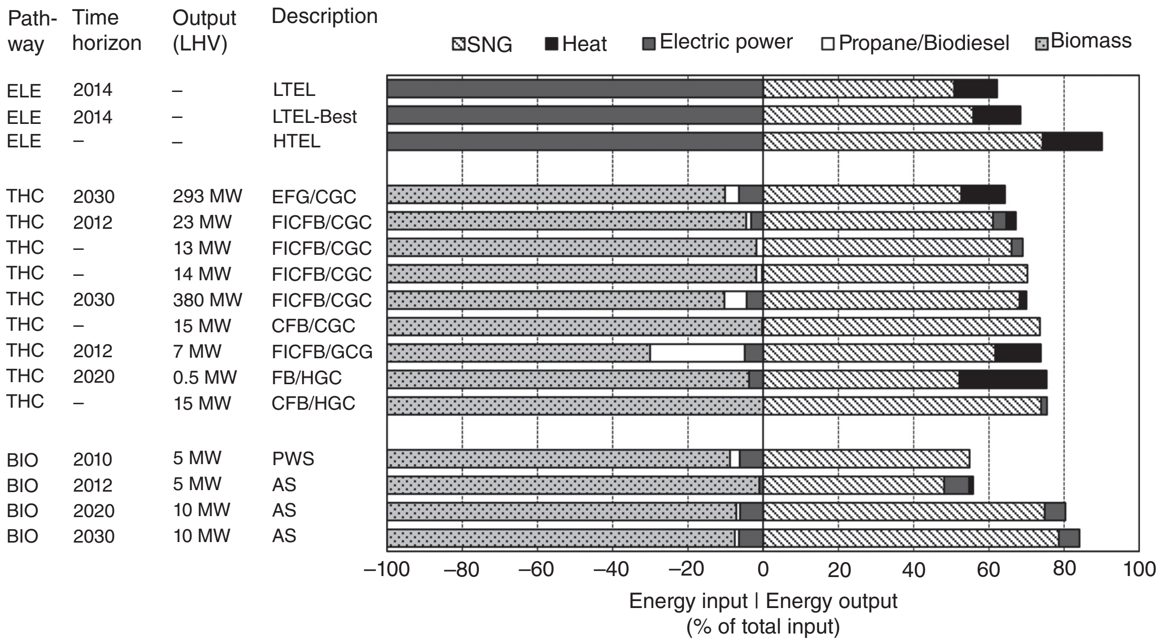

**FIGURE 14** | Comparison of energy input and output of the three SNG pathways [LTEL/HTEL = low/high temperature electrolysis, EFG = entrained flow gasification, (FI)CFB = (fast internally) circulating fluidized bed gasification, CGC/HGC = cold/hot gas cleaning, PWS = pressurized water scrubbing, AS = amine scrubbing)[46,59,68,70,81–86]].

State-of-the-art biogas plants achieve efficiencies in the range of 55–57%.[81,82] However, Müller-Langer et al.[82] expect a strong efficiency increase in the mid-term due to more efficient enzymes and by energetic utilization of the fermentation residues in a biomass power plant. Beside the fermentation process, the main energy loss results from the upgrading of biogas to SNG. The specific electrical energy consumption ranges from 0.2 to 0.3 $kWh_{el}/Nm^3$ of raw gas for an established technology like PSA, water scrubber, or membrane separation and varies strongly with the scale of the upgrading unit. Amine scrubbers have a lower electrical energy demand of 0.12–0.14 $kWh_{el}/Nm^3$ but additionally about 0.55 $kWh/Nm^3$ heat at a temperature level of 120–150°C is required for regeneration of the solvent. Besides electric energy demand, efficiency is determined by the methane slip which is in the range of 1.8–2% for PSA, 1% for water scrubbers, 0.1% for amine scrubbers and 0.5% for membranes.[22]

Published efficiencies of thermochemical biomass conversion to SNG vary between 52 and 54%[82,88] for EFG, 64–70%[81–83,88] for FBG with cold gas cleaning and up to 71–75% for fluidized bed with hot gas cleaning.[70,83] The GoBiGas project aims at an efficiency exceeding 65%.[25] EFG achieves relative low efficiencies due to the energy intensive feed preparation as well as the low methane content of the raw product gas. Beside the gasification and gas cleaning technology used, efficiency is mainly affected by the amount of heat extraction.

As far as the electrochemical pathway is concerned, the efficiency variation is strongly determined by the electrolyser efficiency and the electrolyser technology used. State-of-the-art low-temperature electrolysers reach specific energy consumptions of 4.3–4.5 $kWh/Nm^3{}_{H2}$ corresponding to an efficiency of 70–67% with reference to the lower heating value of $H_2$.[46,59,84] Future high-temperature electrolysers operated at thermoneutral voltage, where the heat production by internal losses is utilized for the electrochemical reaction, can achieve almost 100% efficiency (plus auxiliary consumption for pumps and control). Thereby the overall conversion efficiency to SNG can be enhanced to up to 78.1%[85] compared to about 50–65% for low-temperature electrolysis (89,90 and own calculations based on Refs 46,59,68,84,86). The energy demand for $CO_2$ supply by sequestration from other power plant or industrial processes has a limited influence. The specific energy consumption varies between zero if it is assumed that $CO_2$ is available as a by-product from other processes (e.g., biogas upgrade) and 0.1–0.35 $kWh/kg_{CO2}$[86] for industrial processes, which reduces the overall efficiency by 1–2%-points (based on an electrolyser efficiency of 70%). Overall efficiency can be further improved by utilization of the by-product oxygen from electrolysis as well as utilization of the high-temperature heat of the exothermal methanation reaction. The first Power-to-Gas plant realized by the company Solarfuel (now Etogas) in 2009 with a capacity of 25 $kW_{el}$ achieves an overall efficiency of 40% which was improved to 54% in the 6 $MW_{el}$ plant in Werlte commissioned in 2013.[91]

## Economics

Economic analysis, evaluation, comparison, and discussion of SNG production options prove difficult due to the limitations caused by the different stages of development of the technologies.

Since the biochemical pathway is already TRL 9, full economic analysis can be carried out with high data quality obtained by observing the market over the last couple of years. Economical reviews and market evaluations are carried out by various research groups.[17,82,92,93] In the case of the thermochemical pathway, there are only a few projects in operation, with almost no economic data published yet, leaving economic considerations to difficult prediction and simulation-based analysis. Single process steps have to be analyzed separately to gain knowledge of possible production costs of the overall process now and predicted ones when TRL levels might be increased in the future. However, literature review shows a broad range of approaches to economic analysis of the thermochemical pathway.[29,94–96] Electrochemical SNG production with the lowest TRL can be compared to the thermochemical option in terms of available data, although fewer and less complex process steps enhance prediction accuracy and simplicity. In contrast to the other options, however, economic considerations of the electrochemical pathway heavily depend on the business model applied and the basic assumptions regarding, e.g., the operating hours of the plant.[4,46,59,66,84,97]

In order to compare technologies reasonably, specific productions costs from input/feedstock to feed-in SNG are used as well as specific investment costs based on the HHV. All data is leveled and in case of ranges, mean values are taken for further comparison. Calculated values are based on SNG output. Missing values have been calculated based on simplifications (SNG output was calculated based on raw-biogas output, efficiency of the $CO_2$ separation technology and heating values). Main factors of influence for economic evaluation are the full-load operation hours, the time horizon (projected operation year as well as year of publication) and the scale of the plant.

### *Specific Production Costs SNG*

The cost structure of biochemical SNG production has been extensively examined in several studies and scientific papers with numerous existing commercial plants in operation in Germany and abroad. Figure 15 shows the overview of reviewed data on biochemical SNG production.

Costs are arranged based on the year of initial operation of the plants (projected) with no differentiation between data sources. Mean specific production costs vary between 5.9 and 13.7 €ct/$kWh_{SNG}$ whereas good correlation and data consistency can be found on the range and spread of production costs. The average value for biochemical SNG production is 8.0 €ct/$kWh_{SNG}$. Highest values can be seen based on past data from 2005 to 2010. Future process optimization and increase of plant size to around 10 $MW_{SNG}$ leads to predicted production costs of approximately 6 €ct/$kWh_{SNG}$. All literature sources show good correlation and small production cost spread. Diverse technology differences, mainly $CO_2$ separation technologies, account for only small deviations in overall production costs.

Two general trends are apparent:

- Specific production costs decrease with increasing plant scale (e.g., from 8.8 to 6.2 €ct/$kWh_{SNG}$)
- Specific production costs decrease with considered time horizon (e.g., from 13.7 to 8 €ct/$kWh_{SNG}$)

Technological specifications and influencing factors like different feedstock or special waste treatment facilities are not accounted for in the evaluation although these factors may have significant impact on production costs. For example the digestion of manure leads to lower feedstock costs compared to energy crops due to their inherent lower or even negative raw material costs. However, in many cases, lower feedstock costs are balanced by additional higher gas cleaning costs.

Fewer and less reliable data is available on thermochemical and electrochemical pathways. However, comparison of the pathways shows some significant differences and general trends. Figure 16 shows a double logarithmic graph of the mean specific SNG production costs with plant scale (SNG output in MW).

Following general conclusions can be drawn from the data evaluation: Cost regressions with increasing plant scales are in the same order for all pathways with steepest decrease for thermochemical pathway, which highlights the potential of scale-up for thermochemical SNG production plants. Evaluated scales are in the range of 0.5–380 $MW_{SNG}$,

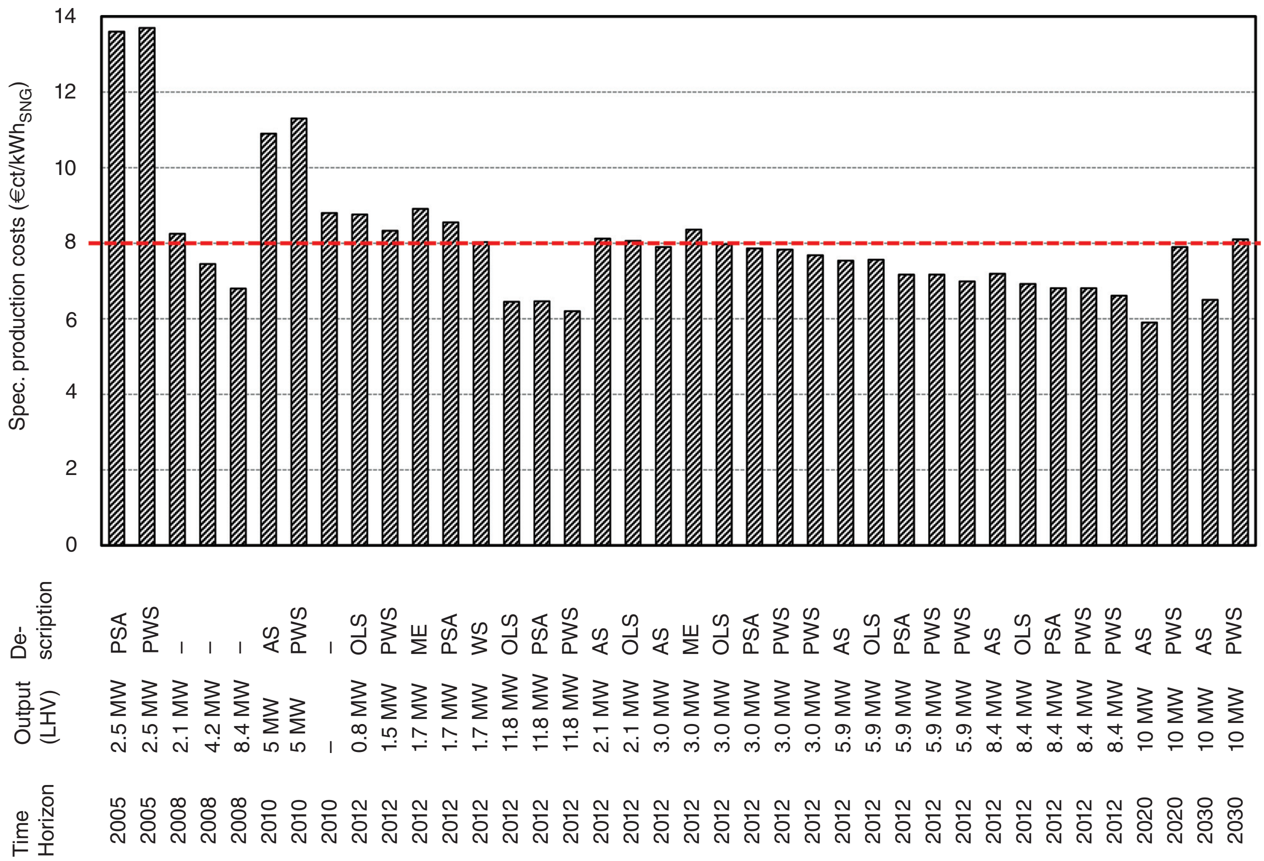

**FIGURE 15** | Overview of specific biochemical SNG production costs in €ct/kWh$_{SNG}$ with varying time horizons (year), plants scales (SNG output) and $CO_2$-separation technologies. PSA, pressure swing adsorption; PWS, pressurized water scrubbing; AS, amine scrubbing; OLS, organic liquid scrubbing; ME, membrane separation.[17,82,92,93,98]

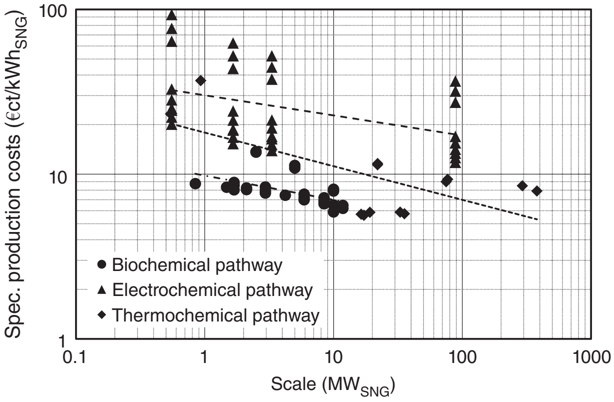

**FIGURE 16** | Mean specific production costs for SNG produced via the three pathways with trend lines.

whereas only thermochemical plants are projected in a scale exceeding 100 MW$_{SNG}$. Biochemical pathway shows only limited up-scale potential and thus only small cost reduction potential. Thermochemical and electrochemical pathways have a potential broad range of scales and scaling effects on the proposed production costs, respectively. The order of specific production costs is: BIO < THC < ELE. Biochemical pathway has lowest production cost range from 5.9 to 13.7 €ct/kWh$_{SNG}$ but scales up to maximum 10 MW are projected due to the low energy density of the feedstock. Thermochemical pathway shows a broad range of calculated production costs from 5.6 to 37 €ct/kWh$_{SNG}$ over a wide range of scales. The electrochemical pathway has the highest costs (8.2–93 €ct/kWh$_{SNG}$) but with a high degree of uncertainty due to the early stage of process development and estimated full-load hours. Overall, the electrochemical option today and in the near future will not be economically competitive. The thermochemical pathway might be competitive in the future favoring large-scale applications in the range above 10–100 MW. The biochemical pathway finally with its established technology can still only survive due to incentives as long as NG prices are not rising significantly.

## Specific Investment Costs SNG

Figure 17 shows the evaluated investment costs. The trends observed for production costs can be seen here again. Increasing plant scale leads to lower specific investment costs. However, most spread can be seen for the thermochemical and electrochemical option indicating uncertainties in the economic evaluations and varying concept approaches.

Mean investment costs for biochemical pathway are about 1300 €/kW$_{SNG}$, for thermochemical SNG production 2600 €/kW$_{SNG}$ and for the electrochemical pathway 3300 €/kW$_{SNG}$, however this mean values are taken including all time frames and all evaluated data sets which limits the significance of these values. Table 7 shows the overview of observed data sets with mean values.

Investment costs around 1000 €/kW$_{SNG}$ should be targeted for all technologies. However, the overview and evaluation of published data sets is not supposed to deliver a general statement which partly is not possible today but rather gives an overview of ranges discussed today and for the future. Besides plant scales, various factors have a significant influence on economics which are not discussed here due to the high complexity and limited comparability of the concepts.

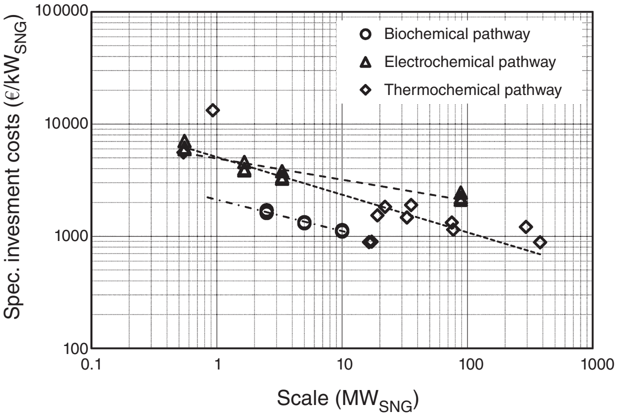

**FIGURE 17** | Mean specific investment costs for SNG production via the three different pathways.

## CONCLUSION

SNG produced from renewable energies either by fermentation (biochemical) or gasification (thermochemical) of biomass with subsequent gas upgrade or from wind and PV via water electrolysis and methanation (electrochemical) can play a key role in a future renewable-based energy system. Owing to the existing infrastructure for storage, distribution, and utilization, renewable SNG can support efforts to guarantee a secure energy supply without greenhouse gas emissions from fossil power plants. In the present review the production processes of the three abovementioned renewable production pathways of SNG are explained and compared in terms of market maturity, efficiency, and economic potential.

While the biochemical pathway is established on a commercial scale, the thermochemical and electrochemical routes are still in the pilot-plant phase. Biochemical production of SNG reaches efficiencies in the range of 55–57% but with a mid-term potential of above 80% due to improved enzymes and energetic utilization of the fermentation residues. In comparison, higher efficiencies of currently up to 70% for the thermochemical pathway are expected, with future improvement up to 75% by applying hot gas cleaning. Electrochemical production achieves efficiencies in the range of 54–60%. Higher efficiencies of up to 78% are expected for HTEL. This means that the highest efficiencies are given for the thermochemical pathway at the moment, followed by the electrochemical and biochemical pathways.

Economic evaluation reveals, that in general, specific production and investment costs decrease with time horizon and increasing scale of the plant. Specific production cost levels vary between 5.9 and 13.7 (biochemical), 5.6–37 (thermochemical), and

**TABLE 7** | Overview of Mean Values and Ranges for All Data Sets (data from Refs 4,17,29,60,66,82,93–95,97–99)

| Pathway | Mean specific Investment Costs [€/kW$_{SNG}$] | Mean Specific Production Costs [€ct/kWh$_{SNG}$] | Time of Initial Operation | Year of Publication | SNG Output [MW] |
|---|---|---|---|---|---|
| Biochemical | 1303 | 8.0 | 2012 | 2013 | 5.6 |
| (range) | 1103–1705 | 5.9–13.7 | 2005–2030 | 2009–2014 | 0.8–11.8 |
| Electrochemical | 3327 | 27.3 | 2014 | 2013 | 23.5 |
| (range) | 625–7052 | 8.2–93.0 | 2010–2035 | 2011–2014 | 0.6–88.5 |
| Thermochemical | 2597 | 11.3 | 2015 | 2009 | 76.3 |
| (range) | 883–13,269 | 5.6–37.0 | 2008–2030 | 2008–2013 | 0.5–380 |

8.2–93 €ct/kWh$_{SNG}$ (electrochemical). Mean specific investment costs show similar behavior and vary between 1303 and 3327 €/kW$_{SNG}$.

On the basis of today's NG prices of around 2–3 €ct/kWh$_{NG}$ none of the concepts is able to produce SNG economically. Thus, from a pure economical point of view, SNG production through bio-, thermo-, and electrochemical pathway is not competitive to fossil NG exploitation. However, since the prices for fossil NG are highly fluctuating and predictions for the far future are difficult, SNG from renewable sources can be a sustainable alternative and play an important role in the transition toward future renewable-based energy systems.

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