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A techno-economic assessment of pyrolysis processes for carbon capture, hydrogen and syngas production from variable methane sources: Comparison with steam reforming, water electrolysis, and coal gasification

Ahmet Çelik, Iadh Ben Othman, Yannik Neudeck, Olaf Deutschmann*, Patrick Lott*

Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstr 20, 76131 Karlsruhe, Germany

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ABSTRACT

The economic and ecologic feasibility of thermal pyrolysis processes with the feedstocks natural gas (H_2 and carbon as products) or biogas (syngas and carbon as products) are studied for different locations – China, USA, Germany, Saudi Arabia, and Türkiye – and compared with state-of-the-art steam reforming and water electrolysis. At all considered locations, the current power generation still causes significant CO_2 emissions between 0.36 and 0.70 kg CO_2e/kWh, leading to CO_2 emissions of H_2 production *via* water electrolysis of more than 18 kg CO_2e/kg H_2. In contrast, due to a lower energy demand, the thermal pyrolysis of natural gas allows for H_2 production with considerably less CO_2 emissions between 6 and 12 kg CO_2e/kg H_2. With a hypothetical power generation relying exclusively on renewable sources, thermal pyrolysis can produce H_2 with approx. 2 kg CO_2e/kg H_2 (originating from natural gas production), which is ecologically more favorable than steam reforming with carbon capture and storage. Furthermore, the H_2 production costs from thermal pyrolysis of natural gas are lower than from electrolysis and steam reforming for locations with low natural gas and electricity costs. For instance, in the USA and Saudi Arabia, H_2 can be produced for less than 1 €/kg H_2. Using biogas as feed for a thermal pyrolysis process even leads to negative CO_2 emissions of up to −1.28 kg CO_2e/kg syngas if the electricity supply is provided from renewable sources, which transforms the process to an active CO_2 sink. However, a potential biogas-to-syngas process cannot compete with state-of-the-art steam reforming in terms of production costs, mainly due to high biogas prices and significantly lower production capacities. In summary, natural gas pyrolysis can be an economically and ecologically feasible alternative to large-scale steam reforming and water electrolysis, especially if prices for the produced carbon exceed 500–1000 €/t. Moreover, a decentralized framework of biogas pyrolysis plants can serve as a feasible CO_2 sink when valuable, sustainable syngas and carbon are produced.

1. Introduction

The pyrolysis of methane-containing feedstocks is a promising method for carbon dioxide-free hydrogen (H_2) production and carbon fixation and is therefore considered a potential climate-friendly alternative to steam reforming and a cost-effective alternative to water electrolysis [1–5]. However, since typically high temperatures are required to decompose the methane (CH_4) molecule, certain requirements must be fulfilled in this context. First, the pyrolysis reactor should be heated using renewable energy sources to eliminate direct carbon dioxide (CO_2) emissions. Second, also indirect emissions need to be considered for a holistic ecological assessment. Herein, the methane source has a significant impact on the CO_2 footprint of the overall process chain and the feed can even affect the products. For instance, while the pyrolysis of natural gas yields solid carbon and gaseous hydrogen, the pyrolysis of biogas results in the formation of syngas, which is a mixture of H_2 and CO. The latter process can even result in negative CO_2 emissions, making it a potential CO_2 sink [6]. In contrast, conventional hydrogen production routes, such as steam reforming and coal gasification, cause CO_2 emissions, which can only be reduced by carbon capture and storage (CCS) technologies. For this, CO_2 is typically separated from the exhaust gas of the production plant in a first step and then stored in a second step, e.g. by injection into suitable geological formations, usually underwater [7].

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* Corresponding authors.
E-mail addresses: deutschmann@kit.edu (O. Deutschmann), patrick.lott@kit.edu (P. Lott).

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The endothermic decomposition of methane according to Equation 1 (reaction enthalpy referring to graphitic carbon) can be realized in thermal processes [8–11], catalytically on metal-based systems [12,13], or by using carbon as catalyst [14,15,8]. While metal-based catalysts enable reasonable CH_4 conversion already at lower temperatures ($<$ 800 °C) [12,13], thermal operation ensures the production of pure carbon without metallic impurities and makes regular catalyst regeneration redundant, but requires higher temperatures well above 1000 °C [8,16]. The use of carbon as a catalyst combines both advantages and thus enables a quasi-autocatalytic process in which the carbon grows primarily on the carbon particles provided initially [17,18,8]. Furthermore, various reactor configurations were suggested, which differ primarily in their energy supply and particle flow control. These include plasma torches [19,20], liquid salt or liquid metal-based systems [21,22], microwave-based systems [23], moving or packed bed systems [24,25], and flow reactors [8,9]. All these approaches aim at an acceleration of the reaction mechanism that comprises radical formation, dehydrogenation and coupling steps, and the suppression of undesired byproduct formation that result from incomplete dehydrogenation [9,26–33].

$$CH_4\ (g) \rightarrow 2H_2\ (g) + C\ (s);\ \Delta_R H^\circ = 75\ \text{kJ mol}^{-1} \quad (1)$$

In addition to entirely technical aspects, an economic and ecological assessment must be considered as well during the design of the overall process. In particular, the chemical feedstocks, the energy sources, and any purification steps before and after the reactor are decisive factors that can depend heavily on external factors such as the location. This request emphasizes the importance of techno-economic studies, which can put the feasibility and profitability of modern pyrolytic production plants in context to conventional processes, such as steam reforming or water electrolysis.

In this regard, some studies have already examined the production costs for hydrogen *via* methane pyrolysis and compared these with reference data for steam reforming and water electrolysis [2,34–38]. Herein, it became clear that methane pyrolysis can be significantly cheaper than water electrolysis and can certainly be economically competitive compared to steam reforming – notably even without considering possible CO_2 taxation [38] – although this depends heavily on other factors, in particular the selling price for the produced carbon [38,39]. The carbon varies significantly: For example, carbon in the form of coke can be sold for 140–370 €/t, carbon black for over 900 €/t, activated carbon for 1800 €/t, graphite for over 9,000 €/t, or in the form of carbon filaments for over 1 million €/t [10,39]. Whether and which forms of carbon can be produced during methane pyrolysis is still the subject to current research [10,40–43]. However, since the conventional methods for carbon black production to date have been emission-intensive furnace processes [44–47], methane pyrolysis would offer the potential to transform this industry into climate-friendliness.

In addition to the carbon price, important factors influencing profitability and the carbon footprint include the energy source, the location and, in particular, the methane source; the latter has been insufficiently studied in previous studies. The current main source of methane is natural gas, which stands out due to its widespread availability, its comparatively low price, but also its greenhouse gas intensive extraction, mainly due to leakages [48,49]. Biogas, on the other hand, is potentially the most environmentally friendly source of methane, because atmospheric CO_2 can be fixed in biomass, whose fermentation and subsequent pyrolysis yields syngas [6]. If the H_2:CO ratio is suitable, this syngas can be widely used in industry. For example, syngas with an H_2:CO ratio of 2:1 can be used to produce methanol, which may then serve as a feedstock in the chemical industry or as a climate-friendly fuel, e.g. in the shipping industry [50]. However, one drawback of using biogas as feedstock is its limited availability, especially compared to natural gas [51]. Therefore, it has not yet been conclusively clarified whether an application in a pyrolysis process is economically reasonable.

As a consecutive step towards a better understanding of the overall process design on an industrial scale, in the present study various thermal pyrolysis processes are investigated with two different methane sources, namely natural gas and biogas. In addition to highlighting the influence of process parameters, in particular the reactor temperature, the influence of external and site-dependent factors, such as costs for feedstock and energy or the carbon sales price, on the production costs and environmental footprint of the respective process are considered. By comparing the results with the respective data for conventional processes, namely steam reforming, electrolysis, and coal gasification, it is studied to what extent and for which locations the pyrolysis of methane or biogas is economically and ecologically feasible.

2. Methods

2.1. Process simulation

The methane pyrolysis process is simulated with the Aspen Plus software (V12; simulation details can be found in the ESI) [52]. The reaction conditions such as temperature, pressure, residence time, and gas composition used for the reactor simulation are based on experimental results from previous publications [6,8,11]. Herein, two different feed gases – natural gas and biogas – were used for investigating thermal pyrolysis processes under industrially viable conditions in a lab-scale high-temperature reactor. For natural gas, a synthetic mixture (SNG, AirLiquide, consisting of 81.2684 vol-% CH_4, 2.9710 vol-% C_2H_6, 0.4913 vol-% C_3H_8, 0.0993 vol-% C_4H_{10}, 14.1600 vol-% N_2, and 1.0100 vol-% CO_2) served as feed in a previous publication [11]; for biogas, a mixture of CH_4 and CO_2 with a molar ratio of 1:1 (common for fermentation processes of agricultural waste [53,54]) was used in a previous experimental study [6].

Irrespective of the feed gas, the process comprises a heating section, a high-temperature flow reactor, a cooling section, and a gas separation as illustrated in the basic flow sheet given in Fig. 1. In the process shown, the feed gas is first preheated to 800 °C by the hot product gas in a heat exchanger. The feed gas is then heated further to reaction temperature using an electric heater before it enters the electrically heated pyrolysis reactor. Herein, a complete separation of the produced carbon from the gaseous products is assumed. The effluent product gas stream enters the heat exchanger where it is cooled to 100 °C with water as cooling medium. Finally, the product gas is purified by means of pressure swing adsorption (PSA) that ensures complete purification.

Although H_2 is known to inhibit thermal CH_4 decomposition [55,56], a dilution of the feed gas stream with H_2 is considered in all simulations. On the one hand, the H_2 content can be used for kinetic control of the pyrolysis reactions and is consequently an effective measure to prevent reactor clogging. On the other hand, it simplifies the downstream gas separation and helps to achieve a H_2:CO ratio of 2:1 in the effluent product gas stream if biogas is used as feed, therefore the dilution ratio depends on the feed gas used.

Since natural gas is typically more abundant than biogas, the volume flow into the system and thus the dimensions of the system are varied. In order to ensure comparability with conventional processes, for natural gas pyrolysis a total feed gas volume flow of 475,000 Nm^3/h is assumed, which is the average feed gas consumption of a steam reforming plant [57]. In contrast, for biogas as feed the sizing correlates to the maximum size of a fermentation plant for biogas production from energy crops or liquid manure. A large biogas plant can commonly produce a maximum of 2000 Nm^3/h of biogas, e.g. with corn silage as substrate; due to long transport routes of the biomass to the fermentation plant, a higher production capacity would be economically disadvantageous [58].

While for natural gas, a molar H_2:natural gas ratio of 2:1 creates balance between avoidance of reactor clogging and inhibition of the decomposition reaction for all temperatures considered herein [11], the H_2 dilution ratio that was used for the techno-economic assessment

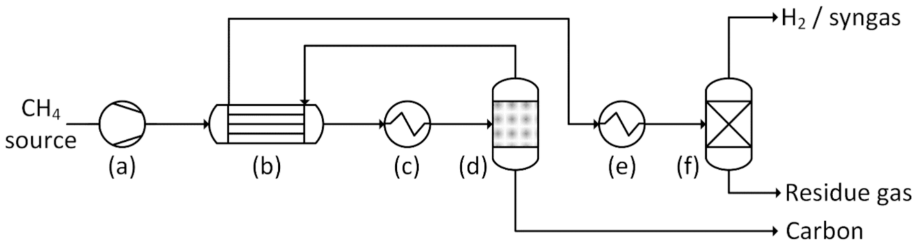

Fig. 1. Basic flow sheet comprising: optional compressor (a), heat exchanger (b), electrical heater (c), reactor (d), cooling (e), gas separation (f).

depends on the reactor temperature for biogas. At temperatures of 1500 °C and above, almost full CH_4 and CO_2 conversion were reported for a feed gas composition with an initial molar CH_4:CO_2 ratio of 1:1 [6]. Therefore, only minimal amounts of H_2 are needed in the feed gas mixture, namely a molar H_2:biogas ratio of 0.1:1, to ensure a molar H_2:CO ratio of 2:1 in the product stream. As the CH_4 and CO_2 conversion decrease for lower reactor temperatures, a molar H_2:biogas ratio of 0.2:1 was assumed at a reactor temperature of 1400 °C and a ratio of 0.3:1 was assumed at 1300 °C, respectively. Consecutively, with a molar H_2:biogas dilution ratio of $\leq$ 0.3:1, the plant was simulated with a feed gas volume flow of 2600 Nm^3/h. Table 1 summarizes the conditions used in the simulations.

Note, that for the sake of simplification the feed gas at the start of the process was assumed to be free of moisture and free of sulfur species. This assumption is particularly relevant for biogas, as the biogas from fermentation can contain up to 3–5 % of water [59]. However, although neither the drying of the biogas nor the desulfurization of the feed gas is simulated in Aspen Plus, both are taken into account as relevant factors in the cost calculation.

2.2. Cost calculation

The total costs are calculated from capital expenditures (CAPEX) and operational expenditures (OPEX) using empiric equations, data from literature, and commercial prices. All costs presented in this study are calculated in euros (€); whenever US dollar ($)-based values needed to be considered in the equations, a conversion factor of 0.92 €/$ was taken into account. To calculate the total CAPEX the costs of the individual components must be determined individually. Herein, the chemical engineering plant cost index (CEPCI) is taken into account individually for each component tracking changes in chemical engineering plant costs over time [60]. Using this index, the costs for upstream H_2S separation is calculated according to Equation (2) [61].

$$C_1\,[€] = \frac{CEPCI_{2023}}{361.3} \bullet 883.2 \bullet \left(\frac{\dot{M}_{in}\,[kg/h]}{2.20462\,kg/h}\right)^{0.7} \tag{2}$$

Herein, C_1 represents the capital costs for the H_2S separation and $\dot{M}_{in}$ the total inlet mass flow. Accordingly, the capital costs for the product purification using PSA are calculated using Eq. (3) [62].

$$C_2\,[€] = \frac{CEPCI_{2023}}{392.6} \bullet 1,389,200 \bullet \left(\frac{\dot{N}_{in}\,[kmol/h]}{500\,kmol/h}\right)^{0.6} \tag{3}$$

Table 2
Reference data and scaling parameter considered for each component.

Component	C_{Ref} (Mio. €)	Scaling parameter	S_{Ref}	Reference
Compressor	0.6	Inlet volume flow	2000 Nm^3/h	[67]
Electrical heater	46	Electrical power	175 MW	[57]
Reactor	2.7	Inlet volume flow	37,000 Nm^3/h	[57,62]
PSA	0.3	Inlet volume flow	2000 Nm^3/h	[61]

C_2 represents the capital costs for the PSA and $\dot{N}_{in}$ the total inlet molar flow. The calculation of the costs for the sorbent of the PSA were calculated separately. In particular, it is assumed that 1 kg sorbent adsorbs 0.01 kmol/h of gas [61] with a cycle time of 1 h, a total number of 4 beds, and a sorbent price of 5.60 €/kg [61]. Furthermore, the costs for both heat exchangers (Fig. 1b and Fig. 1e) are calculated according to Equation (4) [62].

$$C_3\,[€] = \frac{CEPCI_{2023}}{323.8} \bullet 366.16 \bullet \left(\frac{A\,[ft^2]}{1\,ft^2}\right)^{0.65} \bullet 1.52 \tag{4}$$

Herein, C_3 represents the capital costs for the heat exchanger and A the total heat exchange surface area. For the calculation of the heat exchange surface area, usual heat transfer coefficients for a tube-bundle heat exchanger were used [63]. For the remaining components, reference prices are taken from the literature, which are then adjusted to the conditions investigated in this study using a scaling parameter as shown in Eq. (5) [60].

$$C_i = C_{Ref} \bullet \frac{CEPCI_{2023}}{CEPCI_{Ref}} \bullet \left(\frac{S}{S_{Ref}}\right)^{0.6} \bullet F_{Lang} \tag{5}$$

Herein, C_i describes the capital costs of the component, C_{Ref} the reference capital costs, S the scaling parameter used in this study, and S_{Ref} the reference scaling parameter. The values considered for each parameter are given in Table 2. Furthermore, the resulting capital costs are multiplied with an averaged Lang factor F_{Lang} of 7 for methane pyrolysis processes [57,64–66].

Further assumptions were necessary for calculating the annual repayment of the capital costs. For instance, the total investment costs are to be paid off in 15 years and an equity share of 20 % is assumed. The weighted average cost of capital (WACC) was used to calculate the annual interest indicating an average interest rate for debt as well as

Table 1
Overview of assumed feed gas volume flows as well as considered reaction conditions.

Feed gas	Feed volume flow (Nm^3/h)	Reactor temperature (°C)	Residence time (s)	Pressure (bar)	Molar H_2:feed gas ratio
Natural gas	475,000	1000 – 1600	5	1	2:1
Biogas	2600	1300 – 1600	5	1	0.1:1 (≥1500 °C) 0.2:1 (1400 °C) 0.3:1 (1300 °C)

equity. In the present study, a WACC of 6 % was assumed [68]. As the pyrolysis of natural gas or biogas is a continuous process, operation of 24 h a day, 7 days a week is desirable. In order to account for interruptions in the production process that occur throughout the year, e.g. due to maintenance, an annual operating rate of approx. 90 % is assumed, leading to an operating time of 8000 h per year and a maintenance time of approx. 760 h per year; these values were recommended as reasonable assumption for chemical plant operation by Towler and Sinnot [69]. The operational costs of the plant are primarily electricity costs for heating the reactor and the feed gases, further energy costs, as well as the costs for the feed gases itself. Moreover, operational costs include expenses for personnel, maintenance, and insurance, which are all calculated as a percentage of the total operational costs [2,60]. The values for all assumptions made in this context are shown in Table 3.

The sum of the OPEX and the annual repayment of the CAPEX gives the total annual costs of the plant. From this value the revenues from the sale of solid carbon are deducted, whereby within this study the carbon price is varied from 0 €/t (for the case that the carbon cannot be utilized and is only captured) to 2000 €/t (for the case of high-quality carbon black or activated carbon) [10,39]. In order to calculate the hydrogen production costs, the remaining costs are divided by the amount of hydrogen or syngas produced annually.

3. Results & Discussion

The results for the hydrogen or syngas production costs, respectively, and the carbon footprint of the overall process are calculated under consideration of the energy and mass balances from the simulated process as well as the cost calculation methodology described above. The results for both feed gases – natural gas and biogas – are presented below and especially the influence of reactor temperature and external location-dependent parameters, namely costs for feed gas and electricity, are evaluated in detail. Variable carbon prices (0 €/t – 2000 €/t) and three different electricity sources are taken into account: 100 % local electricity mix, 50 % local electricity mix and 50 % electricity from renewable sources, and 100 % electricity from renewable sources. These factors are discussed for five different locations: United States of America (USA), China, Germany, Saudi Arabia, and Türkiye. In order to provide a holistic evaluation for each location that puts the results for the pyrolysis processes into context, the data are compared with other hydrogen or syngas production methods, in particular water electrolysis, conventional steam reforming and coal gasification (in the case of biogas-to-syngas), whereby the latter two processes are considered both with and without CCS. Location-dependent parameters that are assumed for each case based on data from literature, are summarized in Table 4.

3.1. *Natural gas to hydrogen*

3.1.1. *China*

As a first case for this study, local parameters for China were considered. Fig. 2 shows the costs for H_2 production *via* the thermal pyrolysis process described above using fossil natural gas as feed as a function of the reactor temperature. In addition, variable sales prices for the produced carbon as well as different electricity sources are taken into account. Natural gas prices, data for electricity sources and their respective costs as well as the corresponding CO_2 emissions of the power generation are taken from relevant literature [70–72,74]. Also, the corresponding production costs by means of electrolysis and steam reforming (with and without CCS) serve as reference data [49,86,87].

Irrespective of the electricity source, the production costs for H_2 decrease with increasing reactor temperature. This is a direct consequence of the significant increase in CH_4 conversion with increasing temperature while the H_2 selectivities remain relatively constant [6,8,55]. Therefore, the resulting higher amount of H_2 produced compensates for the increased energy demand. Lower reactor temperatures in the range of 1200 °C to 1400 °C become slightly more profitable compared to higher reactor temperatures only if the carbon sales price is 2000 €/t. At these temperatures CH_4 conversions between 55 % and 85 % and H_2 selectivities higher than 95 % can already be achieved [6,8], which may already be sufficient for the design of an industrial process.

In a first step, the current electricity mix in China was considered for a more detailed analysis of the economic competitiveness (Fig. 2a). Currently, over 60 % of the power produced in China originate from coal plants and approx. 35 % from renewable sources; as of 2023, electricity is provided at an average cost of 7.6 €ct/kWh, which correlates with the emission of approx. 0.585 kg CO_2e/kWh [70,74]. If under these circumstances carbon is not sold but only stored (assumed here at 0 €/t), pyrolysis outperforms electrolysis in terms of profitability only at a reactor temperature of 1600 °C. While a carbon price of 500 €/t makes the pyrolysis process competitive at reactor temperatures at 1400 °C and 1600 °C, a carbon sales price of 1000 €/t enables competitive reactor operation already at 1200 °C. With a carbon price of 1000 €/t, hydrogen can be produced for approximately 2 €/kg at 1600 °C, which is competitive with steam reforming. Notably, even negative H_2 production costs would theoretically be possible if a carbon sales price of 2000 €/t could be achieved. However, in this case the solid product would have to meet the requirements of activated carbon and therefore, among other criteria, have a BET surface area of higher than 300 m^2/g [39,88]. These large surface areas are hard to achieve *via* thermal pyrolysis, as carbon deposition can strongly block micropores and consecutively lower the surface area significantly [25]. So, this comparatively high selling price for pyrolytic carbon is not realistic in the short-term, whereby in this respect the application-oriented characterization of pyrolytic carbon and its correlation with reactor operation parameters is still the subject of research [40,89]. Thus, these values should only be used for a prospective comparison.

If the electricity source is changed to a combination of 50 % local electricity and 50 % renewable sources (Fig. 2b), the average electricity price decreases to 5.1 €ct/kWh [71]. This consistently reduces the H_2 production costs *via* thermal pyrolysis. However, the lower electricity price has a much stronger influence on the electrolysis process, which is significantly more energy-intensive compared to natural gas pyrolysis [2]. The production costs for electrolysis are only undercut and comparable to steam reforming at a reactor temperature of 1400 °C and a carbon sales price of 1000 €/t.

The impact of electricity prices is even more significant if 100 % of the electricity originate from renewable sources (as shown in Fig. 2c), which could result in an average electricity price of 2.5 €ct/kWh in China [71]. At this price, electrolysis should be favored over steam reforming as it allows to produce H_2 cost-effectively (with approx. 1.79 €/kg H_2 and appr. 1.96 €/kg H_2 *via* steam reforming without CCS). However, thermal pyrolysis is still profitable at reactor temperatures of 1400 °C and above and a carbon sales price of 1000 €/t, which results in H_2 production costs below 1.50 €/kg. Also, in the scenario that relies on entirely renewable electricity, a hypothetical carbon price of 2000 €/t would enable net-negative H_2 prices for reactor temperatures of 1200 °C and above.

For a 100 % local electricity mix (Fig. 3a), the highest CO_2 emissions of over 20 kg CO_2 equivalents per kg H_2 occur if the pyrolysis reactor runs at 1000 °C. At this operating point, the CO_2 emissions are even significantly higher than those of steam reforming, where approx. 9 kg

Table 3
Assumptions for the cost calculation with their respective value.

Parameter	Assumption	Reference
Amortization period	15 years	Assumed
Equity share	20 %	Assumed
Weighted average cost of capital	6 %	[68]
Operating time per year	8000 h/year	Assumed
Expenses for personnel	2 % of operational costs	[2,60]
Expenses for maintenance	2.5 % of operational costs	[2,60]
Expenses for insurance	4 % of operational costs	[2,60]

Table 4
Summary of local parameters assumed in this study. GER: Germany; SA: Saudi Arabia; TUR: Türkiye.

Location	Natural gas costs (€ct/m^3)	Biogas costs (€ct/m^3)	Electricity costs (€ct/kWh)	Share of fossil fuels in power generation (–)	CO_2 emissions of power generation (kg CO_2e/kWh)	Renewable electricity costs (€ct/kWh)	Refs.
China	36.4	14.9	7.6	65.0 %	0.585	2.5	[70–74]
USA	14.9	22.2	7.6	60.4 %	0.364	2.4	[71,75–78]
GER	55.4	47.9	14.4	45.0 %	0.380	3.9	[71,79–81]
SA	4.3	–	4.4	99.8 %	0.700	3.3	[71,82,83]
TUR	–	21.9	14.9	58.0 %	0.464	4.7	[71,83–85]

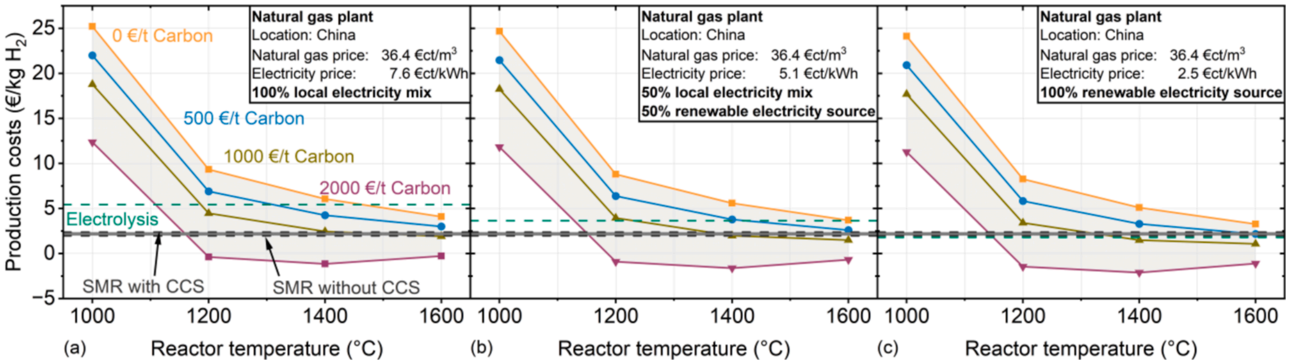

Fig. 2. H_2 production costs via thermal natural gas pyrolysis in China as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Production costs for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

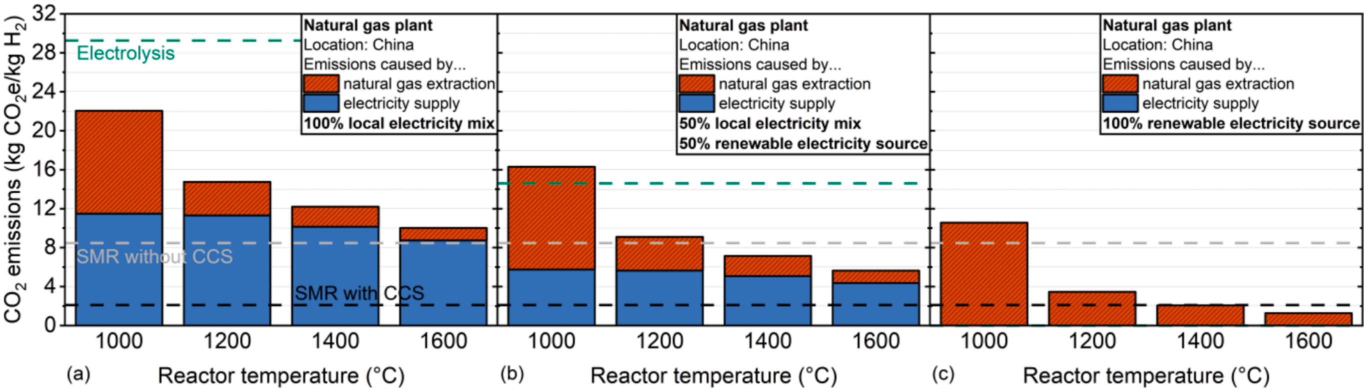

Fig. 3. CO_2 emissions via thermal natural gas pyrolysis in China as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). CO_2 emissions for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

CO_2 equivalents per kg H_2 are released [48,49]. The CO_2 emission values for the pyrolysis process ultimately decrease to 10 kg CO_2 equivalents per kg H_2 due to the substantially higher H_2 yield at reactor temperatures as high as 1600 °C, which is slightly higher than the CO_2 emissions during steam reforming without CCS. Under the assumption of a CO_2 separation of 90 % [49], the CO_2 emissions of the reforming process can even be further decreased below 3 kg CO_2 equivalents per kg H_2 by means of CCS. Compared to water electrolysis, which causes emissions of up to almost 30 kg CO_2 equivalents per kg H_2 with a local electricity mix [74,90], natural gas pyrolysis is advantageous irrespective of the reactor temperature.

Furthermore, if a combination of 50 % renewable electricity sources and 50 % local electricity mix is considered as an energy source (Fig. 3b), this further decreases the CO_2 emissions of natural gas pyrolysis and electrolysis, notably with a stronger impact for electrolysis due to the higher energy demand [90]. Consequently, at a pyrolysis reactor temperature of 1000 °C, the CO_2 emissions from electrolysis are lower than those from natural gas pyrolysis, although at higher reactor temperatures thermal pyrolysis still has lower CO_2 emissions than electrolysis with a minimum of approx. 5 kg CO_2 equivalents per kg H_2 if 1600 °C are chosen for reactor operation. From a reactor temperature of 1400 °C, the direct CO_2 emissions of the pyrolysis process also undercut the emissions from steam reforming (without CCS), which are almost independent of the electricity mix because the energy supply in this process is commonly provided by autothermal combustion [91].

Although the CO_2 equivalents emitted during natural gas extraction remain, the benefits of the pyrolysis process are particularly evident when using 100 % renewable energy sources for the electricity supply. From a reactor temperature of 1200 °C, the CO_2 emissions from natural gas pyrolysis are already approx. four times lower compared to conventional steam reforming without CCS. At a reactor temperature of 1600 °C, even the CO_2 emissions of the steam reforming process with CCS can be undercut, resulting in a minimum of less than 2 kg CO_2 equivalents per kg H_2. However, it must also be mentioned that using a 100 % renewable electricity mix, H_2 production *via* electrolysis no longer causes any direct CO_2 emissions at all, which makes it the most favorable option in principle. Nevertheless, natural gas pyrolysis may still offer economic advantages over electrolysis, as lower H_2 production costs can potentially be realized at high carbon prices (Fig. 2c).

As a summary, thermal natural gas pyrolysis in China can be profitable from a reactor temperature of 1400 °C and higher and at a carbon selling price of 1000 €/t. Herein, both electrolysis as well as steam reforming (with and without CCS) can be undercut economically, even if CO_2 taxation (which would increase the hydrogen production costs *via* steam reforming drastically [92]) is ignored. At the same reactor temperatures, the pyrolysis process can cause less emissions compared to steam reforming (even with CCS), but only if the electricity supply originates from renewable sources.

3.1.2. *United States of America*

Due to comparatively low natural gas and electricity prices as well as a large hydrogen target market [93] the United States can be considered as a particularly attractive location for hydrogen production *via* natural gas pyrolysis. Consequently, it is chosen as a second case that is analyzed in detail within this study. Fig. 4 illustrates H_2 production costs for thermal natural gas pyrolysis in the United States as a function of the pyrolysis reactor temperature with variable sales prices for the produced carbon and for variable electricity sources. Natural gas prices, data for electricity sources and their respective costs as well as the corresponding CO_2 emissions of the power generation are taken from relevant literature [71,77,78]. Furthermore, production costs using electrolysis [90] and steam reforming (with and without CCS) [49] are shown as a reference.

For a simple carbon storage (0 €/t) and a carbon sales price of 500 €/t the H_2 production costs decrease with increasing reactor temperature due to a higher H_2 yield, irrespective of the electricity mix. For a carbon price of 1000 €/t, a further heating of the reactor to temperatures of more than 1200 °C influences the H_2 production costs only marginally and at 2000 €/t the optimum operation temperature is 1200 °C. At the latter carbon selling price, choosing higher temperatures has even a negative influence. Although H_2 yields increase with temperature, it can be concluded that process operation at lower temperatures can be more beneficial if the carbon price is so high that a higher H_2 yield can no longer justify a higher reactor temperature. This is in line with the results for the H_2 production costs at the other locations shown in this work.

Since with 14.9 €ct/m^3 the price of natural gas in the USA is comparatively low, the thermal pyrolysis of natural gas with a 100 % local electricity mix (Fig. 4a) is economically competitive with water electrolysis for reactor temperatures of 1200 °C and above, even without any revenue from the carbon. If the carbon can be sold for 500 €/t or more, the process can even compete with steam reforming if a reactor temperature of 1600 °C at a carbon price of 500 €/t or 1200 °C at a carbon price of 1000 °C is chosen, respectively. A combination of 50 % local electricity mix and 50 % electricity from renewable sources (Fig. 4b) reduces the electricity price by 33 % from 7.6 €ct/kWh to 5.1 €ct/kWh, which has a particularly positive effect on the H_2 production costs *via* water electrolysis, which now fall to below 4 €/kg H_2. However, even in this case, H_2 production *via* thermal natural gas pyrolysis is cheaper, even without any carbon revenue, at reactor temperatures of 1400 °C and above. Furthermore, H_2 prices from steam reforming can be clearly undercut at a carbon sales price of 1000 €/t and from a reactor temperature of 1200 °C with H_2 production costs below 1 €/kg H_2. In this context, the U.S. Department of Energy's “Energy Earthshots Initiative” from 2021 aims to reduce the production costs of clean hydrogen to 1 $/kg within one decade [94]. Accordingly, thermal natural gas pyrolysis could produce hydrogen that fulfills these requirements, even with the current electricity mix.

If 100 % renewable electricity sources with a price of 2.6 €ct/kWh and a carbon sales price of 500 €/t are assumed, the H_2 production costs *via* thermal pyrolysis can compete with those from steam reforming if a reactor temperature of 1400 °C is chosen (Fig. 4c). However, since with such a comparatively low electricity price H_2 can be produced *via* electrolysis for approx. 1.86 €/kg, electrolysis is only slightly more expensive than steam reforming (1.30 €/kg H_2 with CCS) and may be preferred due to the net-zero CO_2 emissions. From an economic point of view, fairly high reactor temperatures as well as carbon sales prices of 500 €/t (at 1600 °C) or 1000 €/t (for temperatures ≥ 1200 °C), respectively, make thermal pyrolysis the cheapest option.

In order to compare the processes also ecologically, Fig. 5 elucidates the resulting CO_2 emissions for thermal natural gas pyrolysis in the United States as a function of reactor temperature with different electricity sources. Data for electrolysis [78,90] and steam reforming (with and without CCS) [49] are given as reference.

The current electricity mix in the USA consists mainly of approximately 60.4 % electricity from fossil sources, 21.3 % from renewable sources, and 18.3 % from nuclear power. This combination of sources is a comparatively CO_2-intensive electricity mix, which causes approximately 0.364 kg CO_2e/kWh [77] and leads to significant CO_2 emissions during H_2 production *via* electrolysis and pyrolysis alike (Fig. 5a). Since water electrolysis requires 5–7 times more energy [90], pyrolytic processes have a clear advantage over electrochemical H_2 production. Furthermore, natural gas pyrolysis can achieve a CO_2 balance that is comparable to that of steam reforming (without CCS) at reactor temperatures of over 1400 °C, with values of around 6 kg CO_2e/kg H_2. The share of natural gas extraction in the total CO_2 emissions per kg of H_2 produced decreases steadily with increasing temperature, irrespective of the electricity supply, because the yield of H_2 increases as well [6,8].

If a less CO_2-intensive electricity supply is assumed, namely a combination of 50 % current electricity mix and 50 % electricity from renewable energies (Fig. 5b), this consequently leads to a drastic reduction in CO_2 emissions from electrolysis by approx. 50 % to approx. 9 kg CO_2e/kg H_2 and thus to a similar CO_2 balance compared to steam

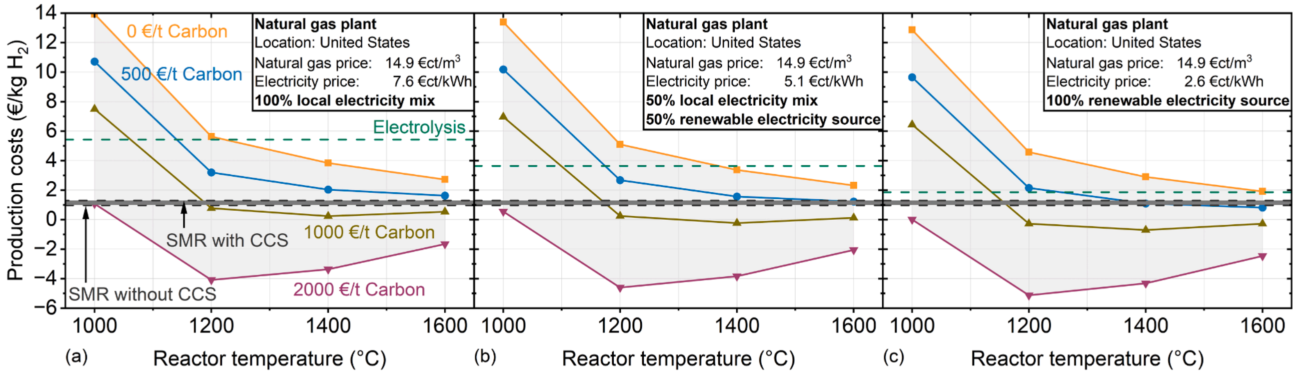

Fig. 4. H_2 production costs via thermal natural gas pyrolysis in the United States as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Production costs for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

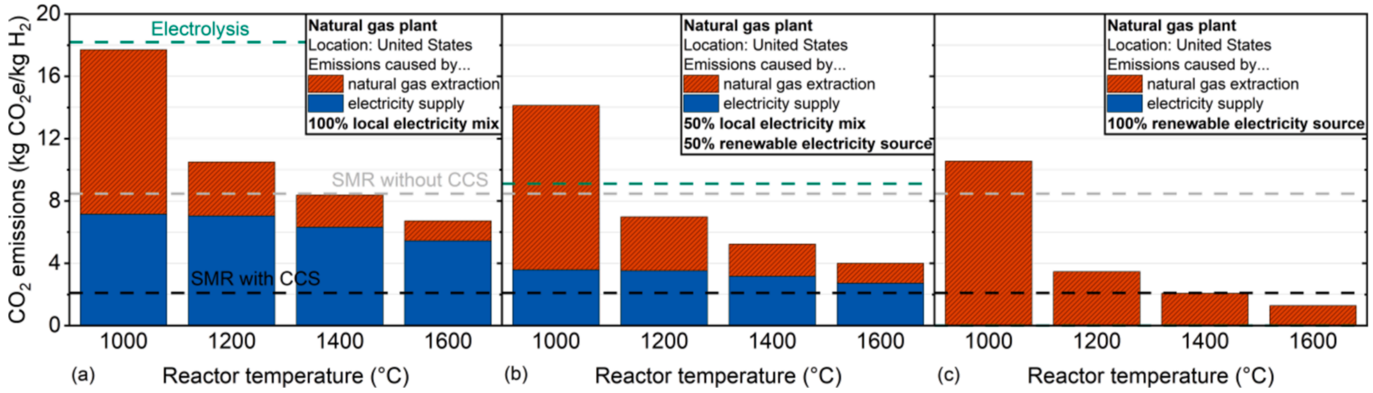

Fig. 5. CO$_2$ emissions via thermal natural gas pyrolysis in the United States as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). CO$_2$ emissions for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

reforming. Although naturally the CO$_2$ emissions from natural gas extraction remain unchanged, the higher share of renewable energy decreases the total CO$_2$ emissions caused by the pyrolysis process. CO$_2$ emissions from natural gas pyrolysis are lower than from steam reforming (without CCS) and water electrolysis already at a reactor temperature of 1200 °C and ultimately reach a minimum of 4 kg CO$_2$e/kg H$_2$ at 1600 °C. Only the combination of steam reforming with CCS can undercut this with an CO$_2$ balance of approx. 2 kg CO$_2$e/kg H$_2$.

Finally, if only CO$_2$-neutral electricity from renewable sources is used (Fig. 5c), the CO$_2$ emissions from pyrolysis result primarily from natural gas extraction, which leads to significantly lower CO$_2$ emissions of around 1 kg CO$_2$/kg H$_2$ at a temperature of 1600 °C and thus even undercuts steam reforming with CCS. However, in this case the CO$_2$ balance of electrolysis, which can potentially produce completely CO$_2$-neutral H$_2$, is unbeaten. Analogous to the findings discussed in the previous chapter, an entirely economically driven process design would still favor the pyrolytic H$_2$ production route over electrolysis, which would likely only change if a price is assigned to CO$_2$ emissions, i.e. as a CO$_2$ tax or certificate.

3.1.3. Germany

Fig. 6 reveals H$_2$ production costs for thermal natural gas pyrolysis in Germany as a function of the pyrolysis reactor temperature with variable sales prices for the produced carbon and for variable electricity sources. Natural gas prices, data for electricity sources and their respective costs as well as the corresponding CO$_2$ emissions of the power generation are taken from relevant literature [71,79,81]. Furthermore, production costs using electrolysis [90] and steam reforming (with and without CCS) [49] are shown as a reference.

Compared to the USA and China, both the natural gas price and the local electricity price are significantly higher in Germany. This generally leads to higher H$_2$ production costs compared to the two countries discussed above. In this context, steam reforming almost always remains the cheapest alternative. With a 100 % local electricity mix, electrolysis is not competitive since H$_2$ prices exceed 10 €/kg. The H$_2$ production costs *via* natural gas pyrolysis only approach those of steam reforming (approx. 2.50 €/kg H$_2$ without CCS and approx. 3 €/kg H$_2$ with CCS) at a reactor temperature of 1600 °C, which is associated with considerable technical challenges, and an assumed carbon sales price of over 1000 €/t.

Decarbonizing the electricity supply reduces the price of electricity. This has a particularly positive impact on electrolysis, which can produce H$_2$ for around 7 €/kg if 50 % of the local electricity mix are replaced by CO$_2$-neutral electricity (Fig. 6b) and even reaches almost the price of steam reforming (with CCS) in the case of 100 % CO$_2$-neutral electricity (Fig. 6c). However, natural gas pyrolysis profits to a lesser extent from lower electricity prices because it is strongly governed by the high natural gas price in Germany. Irrespective of the electricity source, the pyrolysis process under the parameters subject to this study becomes competitive only at a reactor temperature of 1600 °C or if carbon revenues are high.

Fig. 7 illustrates the CO$_2$ emissions caused by for thermal natural gas pyrolysis in Germany as a function of reactor temperature with different electricity sources. Herein, data for CO$_2$ intensity of the electricity sources is taken from literature [81]. Also, data for electrolysis [90] and steam reforming (with and without CCS) [49] is shown as a reference.

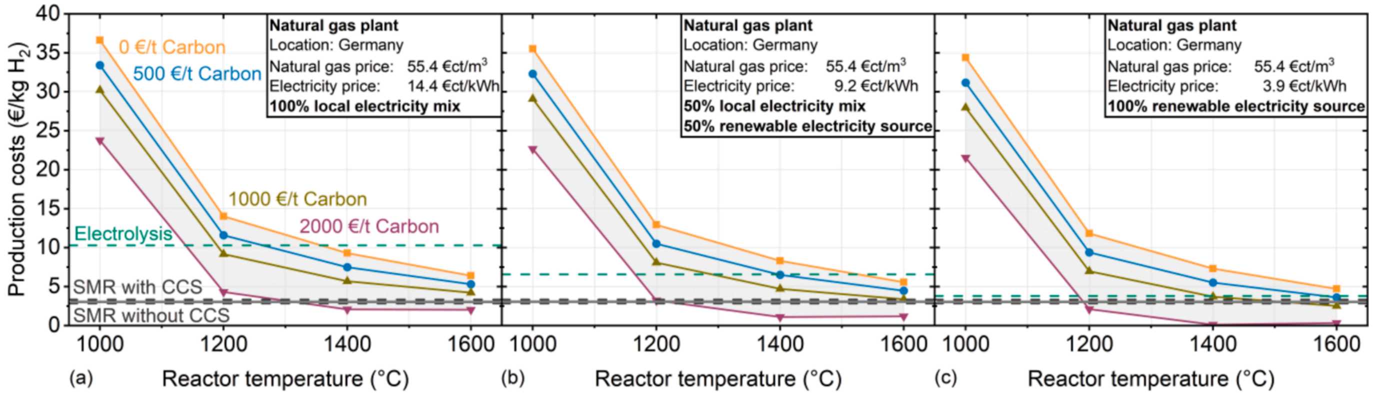

Fig. 6. H$_2$ production costs via thermal natural gas pyrolysis in Germany as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Production costs for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

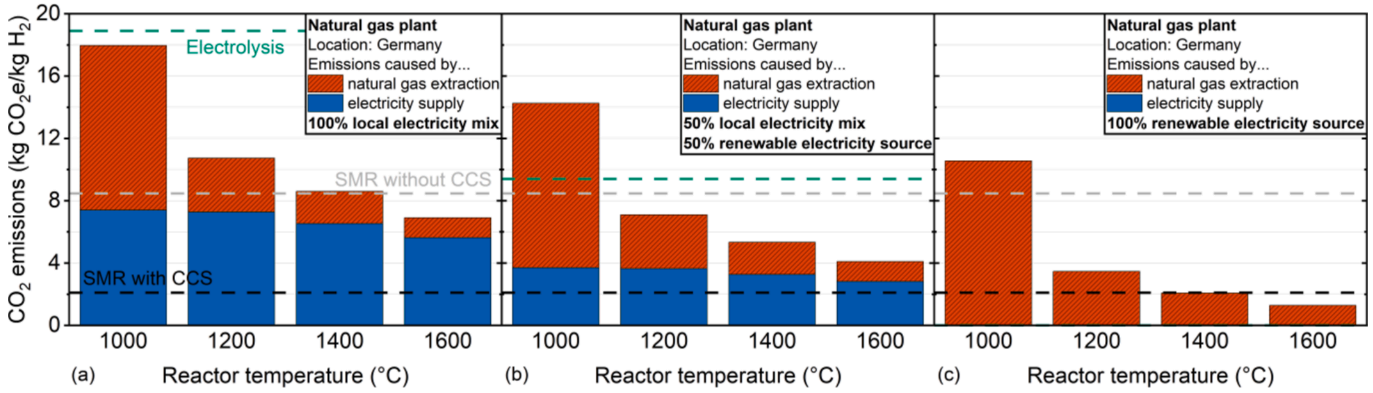

Fig. 7. CO_2 emissions via thermal natural gas pyrolysis in Germany as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). CO_2 emissions for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

Even if already today almost 55 % of the electricity in Germany comes from renewable energies, the supply is still associated with significant CO_2 emissions of appr. 0.380 kg CO_2e/kWh due to a considerable proportion of approx. 27 % of coal-fired power plants [81]. The CO_2 balance of the electricity supply in Germany is therefore similar to that of the USA and thus the trends depicted in Fig. 7 strongly resemble the US-data presented in Fig. 5. With the current 100 % local electricity mix (Fig. 7a), the CO_2 emissions of both electrolysis and natural gas pyrolysis are higher than those of steam reforming (without CCS) and thermal pyrolysis can undercut steam reforming only at a reactor temperature of 1600 °C. With a combination of 50 % local electricity mix and 50 % electricity from renewable sources (Fig. 7b) the CO_2 emissions of electrolysis (approx. 9.50 kg CO_2e/kg H_2) come closer to those of steam reforming (without CCS) of approx. 8.50 kg CO_2e/kg H_2. The CO_2 emissions of natural gas pyrolysis even undercut these values if reactor temperatures of 1200 °C and above are chosen, and reach a minimum of 4 kg CO_2e/kg H_2 at a reactor temperature of 1600 °C. In addition, with an electricity supply from 100 % renewable sources (Fig. 7c), electrolysis can naturally be operated completely CO_2-neutral, whereas natural gas pyrolysis competes with steam reforming with CCS, or even undercuts it at 1600 °C. In general, pyrolysis is therefore particularly suitable as a key H_2 production technology during the decarbonization of the electricity supply. In Germany, it must compete economically and ecologically with electrolysis due to the comparatively high price of natural gas in the case of a completely CO_2-free electricity supply, making the market conditions a particularly challenging economic framework.

3.1.4. *Saudi Arabia*

As the competitiveness of natural gas pyrolysis depends on both the price of natural gas and the price of electricity, countries that have their own natural gas production as well as great potential for power generation from renewable energy sources seem to be particularly suitable locations for establishing large-scale pyrolysis processes. In this respect, Saudi Arabia stands out due to its relatively low costs for energy and natural gas as well as its established chemical industry. Fig. 8 summarizes the H_2 production costs for thermal natural gas pyrolysis in Saudi Arabia as a function of the pyrolysis reactor temperature assuming different sales prices for the produced carbon and under consideration of variable electricity sources. Natural gas prices, data for electricity sources and their respective costs as well as the corresponding CO_2 emissions of the power generation are taken from relevant literature [71,82,83]. Furthermore, production costs using electrolysis [90] and steam reforming (with and without CCS) [49] are shown as a reference.

In Saudi Arabia, electricity is mainly generated in gas and oil power plants (with a share of 61 % and 39 % respectively), which is associated with emissions of approx. 0.7 kg CO_2e/kWh [95]. Among the countries considered for the present study, this is the electricity mix with the highest CO_2 emissions. Since the average cost of electricity is already as low as 4.4 €ct/kWh [82,83], a transformation of the electricity supply has a lower impact on the electricity price compared to the other countries considered herein and reduces the electricity price by only 25 % to 3.3 €ct/kWh if only renewable energy sources are used [71]. As cheap energy meets a comparatively low natural gas price of around 4.3 €ct/m^3, natural gas pyrolysis for H_2 production is economically favored over electrolysis for all energy mixes as long as the reactor temperature is 1200 °C or higher, even without consideration of any revenue from the

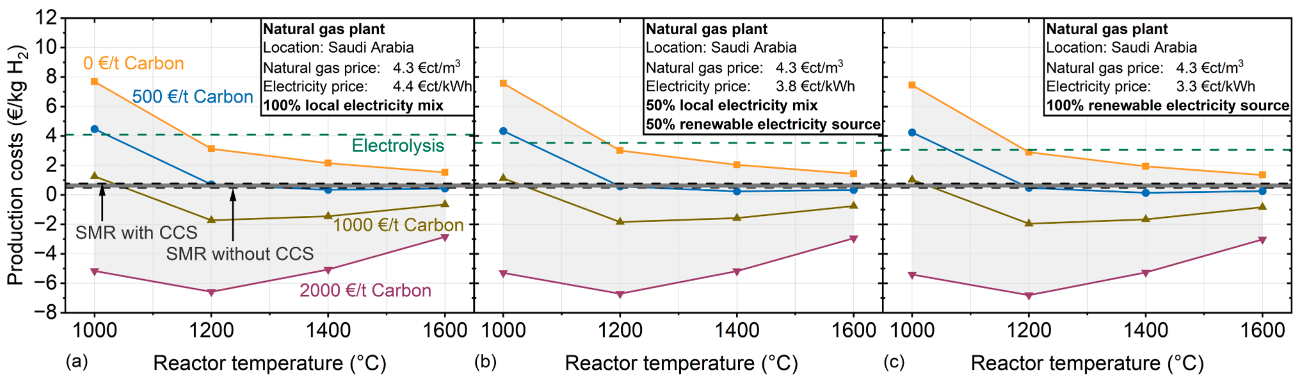

Fig. 8. H_2 production costs via thermal natural gas pyrolysis in Saudi Arabia as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Production costs for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

carbon.

With H_2 production costs of less than 2 €/kg H_2, pyrolysis reactor operation at 1600 °C using the local energy mix (Fig. 8a) is directly competitive with steam reforming (without carbon revenue) or even undercuts it if a carbon selling price of at least 500 €/t is assumed. Water electrolysis, on the other hand, results in H_2 production costs of around 4 €/kg H_2 due to the higher energy requirement. While this value is more than twice as high as the production costs *via* pyrolysis, it is still significantly lower than the H_2 production costs *via* electrolysis using the local energy mix in any other country considered herein. This underscores the suitability of Saudi Arabia as a potential location for H_2 production, both *via* electrolysis and natural gas pyrolysis, already nowadays. Remarkably, negative H_2 production costs can occur for all electricity mixes subject to this study if the carbon selling price is assumed to be at least 1000 €/t (green curves in Fig. 7a-c). The process simulations predict local minima in H_2 production costs for a reactor temperature of 1200 °C and a carbon price of 1000 €/t and 2000 €/t, and a hypothetical global minimum of −6.80 €/kg H_2 for reactor operation at 1200 °C and a carbon price of 2000 €/t with renewable energy (Fig. 8c).

As electricity generation in Saudi Arabia is currently coupled to high emissions, CO_2 balances for all processes need to be considered. Therefore, Fig. 9 shows the CO_2 emissions resulting from thermal natural gas pyrolysis in Saudi Arabia as a function of reactor temperature with different electricity sources. Data for electrolysis [90] and steam reforming (with and without CCS) [49] are shown as a reference.

Due to the comparatively CO_2-intensive electricity supply, energy-intensive electrolysis, unless electricity from 100 % renewable sources is used, consistently causes more CO_2 emissions compared to steam reforming and pyrolysis, with up to 35 kg CO_2e/kg H_2 (for a 100 % local electricity mix, Fig. 9a). Natural gas pyrolysis, on the other hand, is more CO_2 intensive than steam reforming with the current electricity mix. This means that both alternative H_2 production routes would currently cause more emissions compared to the conventional route (Fig. 9a). Natural gas pyrolysis can only come close to steam reforming from an ecological perspective if a power supply from 50 % of the current electricity mix and 50 % renewable sources is chosen along with reactor temperatures of 1200 °C and above (Fig. 9b). With less than 2.5 kg CO_2e/kg H_2 steam reforming with CCS is the least CO_2-intensive route with this electricity mix. In the scenario with 100 % renewable sources, pyrolysis can undercut steam reforming with CCS in terms of CO_2 emissions for reactor temperatures of 1400 °C and above (Fig. 9c).

In summary, hydrogen can already be produced comparatively cheap in Saudi Arabia, regardless of the production method. However, if the global climate targets are taken into account that aim at avoiding CO_2 emissions as much as possible, a drastic decarbonization of the power supply is required. Otherwise, state-of-the-art steam reforming with almost 9 CO_2e/kg H_2 will remain more climate-friendly than electrolysis and pyrolysis. In contrast to electrolysis, natural gas pyrolysis can outperform steam reforming not only ecologically but also economically if the carbon produced can be sold for more than 500 €/t.

3.1.5. Summary

In order to compare the case studies discussed in detail above, Table 5 summarizes the H_2 production costs *via* natural gas pyrolysis, electrolysis (each with a 100 % local electricity mix and electricity from

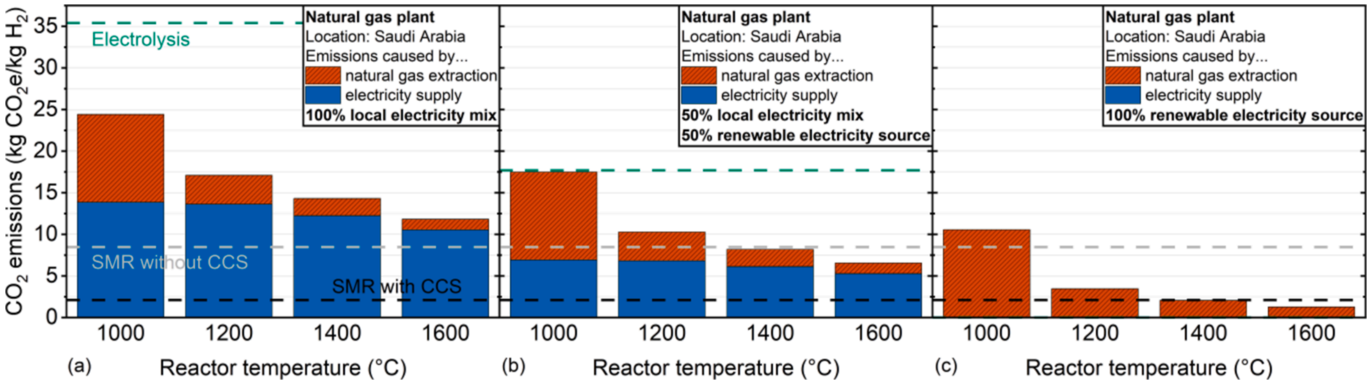

Fig. 9. CO_2 emissions via thermal natural gas pyrolysis in Saudi Arabia as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). CO_2 emissions for electrolysis and steam reforming (with and without carbon capture) are shown as reference.

Table 5
Costs for hydrogen production via natural gas pyrolysis with a 100% local electricity mix and a theoretical 100% electricity supply from renewable sources at a carbon selling price of 500 €/t and 1000 €/t. The corresponding reactor temperature is given in brackets. Data for hydrogen production costs via electrolysis and steam reforming (without (w/o) and with (w/) CCS) is shown as reference. GER: Germany; SA: Saudi Arabia.

Minimum H_2 production costs (€/kg H_2)						
Country	Pyrolysis		Electrolysis		Steam reforming	
					w/o CCS	w/ CCS
	Local e-mix	Renewable electricity	Local e-mix	Renewable electricity	Independent from e-mix	
H_2 production costs (€/kg H_2) at a carbon selling price of 500 €/t carbon						
China	3.00 (1600 °C)	2.17 (1600 °C)	5.43	1.79	1.96	2.37
USA	1.63 (1600 °C)	0.82 (1600 °C)	5.41	1.86	0.97	1.30
GER	5.31 (1600 °C)	3.61 (1600 °C)	10.29	3.79	2.84	3.32
SA	0.35 (1400 °C)	0.48 (1200 °C)	4.02	3.06	0.48	0.77
H_2 production costs (€/kg H_2) at a carbon selling price of 1000 €/t carbon						
China	1.91 (1600 °C)	1.49 (1400 °C)	5.43	1.79	1.96	2.37
USA	0.78 (1200 °C)	−0.27 (1200 °C)	5.41	1.86	0.97	1.30
GER	4.22 (1600 °C)	2.52 (1600 °C)	10.29	3.79	2.84	3.32
SA	−1.72 (1200 °C)	−1.95 (1200 °C)	4.02	3.06	0.48	0.77

100 % renewable sources), and steam reforming (with and without CCS) for each country. The production costs are given under the assumption of carbon sales prices of 500 €/t and 1000 €/t. These prices were selected on the basis of previous publications, which investigated the feasibility of a carbonaceous fixed bed during pyrolysis and which provide first implications on the quality of the accruing carbon [6,25]. In particular, acetylene coke was used, which could potentially be marketed as a form of carbon black for the above-mentioned prices. Regarding the production costs *via* thermal pyrolysis, the corresponding reactor temperature is given as well. This reactor temperature corresponds either to the lowest temperature at which the pyrolysis process undercuts other technologies in terms of price levels, or, if natural gas pyrolysis cannot compete with the conventional methods, the reactor temperature corresponds to the lowest production costs that could be achieved at with the respective electricity mix. Note, that as already discussed in previous chapters, it was assumed that the H_2 production costs *via* steam reforming are independent of the electricity mix, as the reactor commonly is heated by autothermal combustion [91].

In this comparison, Saudi Arabia stands out with the by far lowest H_2 prices derived from the cases considered in the present study: With the current local electricity mix and with a comparatively low carbon selling price of 500 €/t, production costs of H_2 as low as 0.35 €/kg H_2 can be achieved by means of pyrolysis at a reactor temperature of 1400 °C. Among the processes discussed herein, these low costs make pyrolysis the cheapest H_2 production route. Moreover, if a carbon selling price of 1000 €/t is assumed, the thermal pyrolysis process undercuts the costs of all other processes already at a reactor temperature of 1200 °C. With the current electricity mix in Saudi Arabia, negative H_2 production costs as low as −1.72 €/kg would be achieved. Even with 100 % carbon–neutral electricity generation, thermal pyrolysis is economically most viable already at a reactor temperature of 1200 °C, resulting in H_2 production costs of 0.48 €/kg H_2 (500 €/t carbon) and −1.95 €/kg H_2 (1000 €/t carbon), respectively. Only steam reforming without CCS allows to produce H_2 with similar costs, whereas the price for H_2 from electrolysis always exceeds 3 €/kg H_2, irrespective of the energy mix.

The second lowest prices for H_2 from pyrolysis can be achieved in the USA, where at a carbon selling price of 500 €/t production costs of 0.82 €/kg H_2 are possible with renewable electricity and at a reactor temperature of 1600 °C, which is significantly lower than the prices for H_2 from electrolysis (1.86 €/kg) or steam reforming with CCS (1.30 €/kg). If a carbon selling price of 1000 €/t is assumed, a reactor temperature of 1200 °C with renewable electricity (leading to theoretically negative H_2 production costs of −0.27 €/kg H_2) is already sufficient to outperform the alternative technologies economically.

Notably, given the high technology readiness level of pyrolysis processes – for instance, reference is given to BASF's successful operation of a natural gas pyrolysis pilot plant whose setup was completed by the end of 2020 in Ludwigshafen, Germany [96] – prospects are excellent that natural gas pyrolysis will meet the American Hydrogen Shot target defined by the US Department of Energy in 2021, namely producing 1 kg of hydrogen for less than 1 $ within one decade [94]. In conclusion, both the USA and Saudi Arabia are potentially profitable locations for establishing a pyrolysis process.

In China, at a carbon selling price of 500 €/t the minimum costs of H_2 obtained from natural gas pyrolysis with renewable electricity (2.17 €/kg H_2 achieved at a reactor temperature of 1600 °C) are slightly lower than the costs of steam reforming with CCS (2.37 €/kg H_2). However, both processes can be undercut by electrolysis (1.79 €/kg H_2) if the electricity comes from renewable sources. In contrast, the pyrolysis process becomes economically slightly more attractive than electrolysis and steam reforming if a carbon selling price of 1000 €/t is assumed. Since the price difference compared to electrolysis is only marginal, the latter process would be probably be preferred due to its net-zero CO_2 emissions.

In Germany, assuming a carbon selling price of 500 €/t, pyrolysis is always more expensive than steam reforming, both with and without CCS. Furthermore, the production costs of hydrogen by electrolysis (3.79 €/kg H_2) with electricity from renewable sources are only slightly higher than the costs of natural gas pyrolysis (3.61 €/kg H_2). Assuming a carbon selling price of 1000 €/t, pyrolysis becomes theoretically the economically most feasible process with 2.52 €/kg H_2, however a challenging reactor temperature of 1600 °C is needed to achieve these production costs. In general, Germany has by far the highest H_2 production costs of all countries considered within this work. Hence, a potential import of H_2 may be cheaper.

Although in countries such as China or Germany electrolysis seems more viable than other technologies if only economic aspects are taken into account, the CO_2 balance is better only if the power supply is completely emission-free. In comparison, natural gas pyrolysis can emit significantly less CO_2 even with more emission-intensive power supplies due to its lower energy consumption. To analyze this in more detail, Table 6 provides an overview on the CO_2 emissions caused by the overall processes, i.e., natural gas pyrolysis, electrolysis (each with a 100 % local electricity mix and electricity from 100 % renewable sources), as well as steam reforming (with and without CCS), for each country. Regarding the emissions *via* thermal pyrolysis, the corresponding reactor temperature is always given in addition. As discussed above, the lowest emissions can always be achieved if a reactor temperature of 1600 °C is chosen, which is therefore assumed for the case of a local electricity supply. For the case of using renewable electricity, the lowest reactor temperature that enables natural gas pyrolysis to undercut H_2 prices from steam reforming with CCS is assumed, namely 1400 °C. Furthermore, it was assumed that the emissions from steam reforming are independent of the electricity mix, as the reactor is commonly heated by autothermal combustion [91].

With the current local electricity supply, natural gas pyrolysis causes significantly lower emissions compared to electrolysis in all countries considered in this study. In particular, electrolysis causes approx. three times more CO_2 equivalents per kg of H_2 produced compared to thermal pyrolysis. Notably, only an entirely renewable electricity supply will ensure an emission-free production of H_2 by means of electrolysis. With the current electricity mix, steam reforming with CCS is the ecologically

Table 6

Emissions for hydrogen production via natural gas pyrolysis with a 100% local electricity mix and a theoretical 100% electricity supply from renewable sources. The corresponding reactor temperature is given in brackets. Data for emissions via electrolysis and steam reforming (without (w/o) and with (w/) CCS) is shown as reference. GER: Germany; SA: Saudi Arabia.

Emissions (kg CO_2e/kg H_2)						
Country	Pyrolysis		Electrolysis		Steam reforming	
					w/o CCS	w/ CCS
	Local e-mix	Renewable electricity	Local e-mix	Renewable electricity	Independent from e-mix	
China	10.01 (1600 °C)	2.07 (1400 °C)	29.25	0	8.47	2.10
USA	6.72 (1600 °C)	2.07 (1400 °C)	18.20	0	8.47	2.10
GER	6.90 (1600 °C)	2.07 (1400 °C)	18.90	0	8.47	2.10
SA	11.82 (1600 °C)	2.07 (1400 °C)	35.40	0	8.47	2.10

most favorable option for H_2 production, especially in countries with emission-intensive power supplies such as China or Saudi Arabia. In these two countries, pyrolysis causes more emissions than steam reforming without CCS. However, in countries with a comparably low-emission power supply, such as the USA and Germany, natural gas pyrolysis is already ecologically favorable compared to steam reforming without CCS with the current local electricity mix. The advantage becomes even more pronounced if the electricity is supplied from renewable sources; in this case, natural gas pyrolysis (with 2.07 kg CO_2e/kg H_2) can undercut the emissions from steam reforming with CCS (2.10 kg CO_2e/kg H_2) already at a reactor temperature of 1400 °C. Note, that if the reactor temperature is further increased to 1600 °C the lowest limit for natural gas pyrolysis is achieved with 1.28 CO_2e/kg H_2, further increasing the difference to steam reforming. As a conclusion, from an ecological point of view, thermal natural gas pyrolysis offers itself as a bridging technology between current steam reforming and future electrolysis, which becomes ecologically feasible once the power supply is sufficiently decarbonized. However, even if an entirely emission-free power supply is realized, economic considerations may still benefit natural gas pyrolysis because it can be significantly cheaper compared to electrolysis, especially in regions with low costs for natural gas or electricity.

3.2. Biogas to syngas

3.2.1. China

China has a considerable potential for biogas production, with agricultural residues and organic wastes forming the main biomass sources [73,97]. Utilization of the biogas is still discussed, whereby energy generation is currently the main objective of the biogas industry [73]. However, biogas-to-chemicals processes would be much more elegant as they can directly convert CO_2 into value-added chemicals instead of releasing it again during combustion processes, e.g., in combined heat and power plants. In this context, Fig. 10 elucidates syngas production costs for thermal biogas pyrolysis in China as a function of the pyrolysis reactor temperature with variable sales prices for the produced carbon and for variable electricity sources. Local biogas prices, data on electricity sources and their respective costs as well as the corresponding CO_2 emissions of the power generation are taken from relevant literature [70–74]. In addition, corresponding production costs using steam reforming [49] as well as coal gasification, which represents the main syngas production route in China [98], are shown as reference (assuming a constant coal price of 92.26 € [92] for all countries considered in this study). Note, that for the sake of clarity only the results considering CCS are shown throughout this section. The results for conventional syngas production routes without CCS can be found in the ESI.

Due to a large agricultural industry and favorable energy prices, biogas production in China is relatively cheap [73]. Nevertheless, several requirements must be met in order to ensure the profitability of the biogas-to-syngas process. From a technical point of view, a reactor temperature of 1500 °C is required, as this enables not only an almost full conversion for both CH_4 and CO_2 [6], but also results in a H_2:CO ratio of 2:1 and generally represents the operational point with the most favorable syngas production costs. However, the production costs also strongly depend on the electricity price. For instance, with the current local electricity mix (Fig. 10a), carbon selling prices of at least 1000 €/t are required to ensure economic competitiveness with conventional syngas production methods coupled with CCS, which can produce syngas for 0.68 €/kg (steam reforming) or 0.70 €/kg (coal gasification), respectively [92]. With a combination of 50 % local electricity mix and 50 % electricity from renewable sources (Fig. 10b), costs for syngas production *via* thermal pyrolysis of less than 0.80 €/kg can be achieved at a carbon sales price of 500 €/t and at reactor temperatures of 1500 °C and higher. Only when electricity is provided from 100 % renewable sources (Fig. 10c), which corresponds to an electricity price of 2.5 €ct/kWh, thermal pyrolysis ends up roughly at the same price level as steam reforming and gasification, both coupled with CCS, at a carbon selling price of 500 €/t. Without commercialization of the carbon (corresponding to 0 €/t carbon), the process remains more expensive than conventional syngas production methods. However, this could change in the case of CO_2 taxation, which is not considered in this work but that has the potential to increase the price for syngas obtained from coal gasification by a factor of two [92].

Avoiding CO_2 emissions is therefore the essential advantage of biogas pyrolysis, as for instance a potential carbon sink can be realized through the conversion of CO_2 [6]. The overall CO_2 balance, however, depends strongly on external and process parameters. Therefore, Fig. 11 shows the resulting CO_2 sources and sinks due to electricity supply, H_2 dilution (assumed to be supplied *via* SMR with CCS, in order to ensure a H_2:CO ratio of 2:1 in the product gas), CO_2 fixation by biomass as well as the total CO_2 balance for thermal biogas pyrolysis in China as a function of the reactor temperature and for different electricity sources. Data for syngas production *via* steam reforming and coal gasification (both with CCS) is shown as reference [92].

Assuming the local, comparatively emission-intensive electricity supply with 0.585 kg CO_2e/kWh [74], the hypothetical biogas plant still produces approx. 0.4 to 0.6 kg of CO_2 equivalents per kg of syngas produced with the current Chinese electricity mix (Fig. 11a). The CO_2 sink due to the carbon fixation in the biomass cannot compensate these emissions. If CCS is used, however, the CO_2 emissions from steam reforming and coal gasification are approx. 0.2 kg CO_2e/kg syngas lower than those from biogas pyrolysis. Only when the electricity supply is at least partly decarbonized, the overall CO_2 balance for biogas pyrolysis

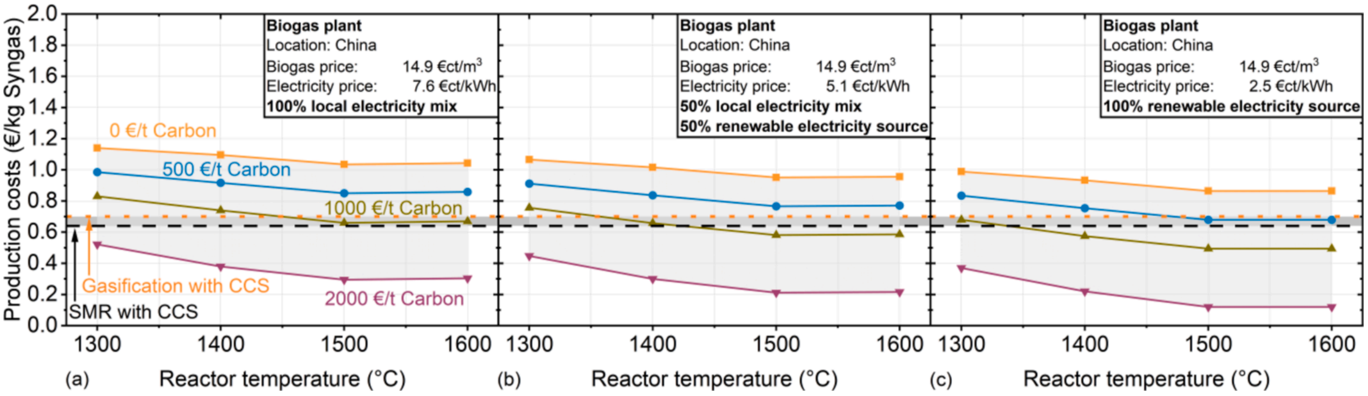

Fig. 10. Syngas production costs via thermal biogas pyrolysis in China as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average production costs for syngas via steam reforming and coal gasification (both with CCS) are shown as reference.

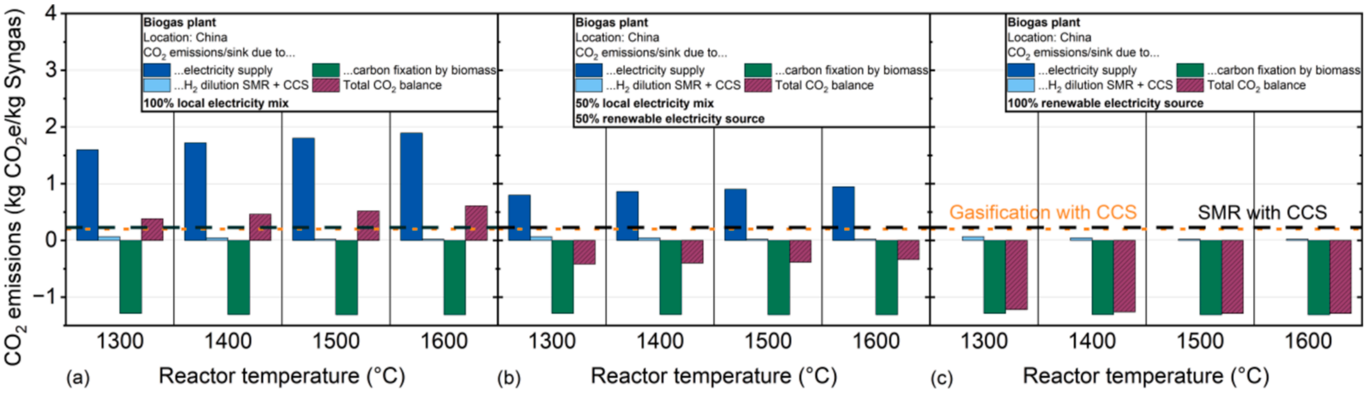

Fig. 11. CO_2 emissions via thermal biogas pyrolysis in China as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average CO_2 emissions for syngas production via steam reforming and coal gasification (both with CCS) are shown as reference.

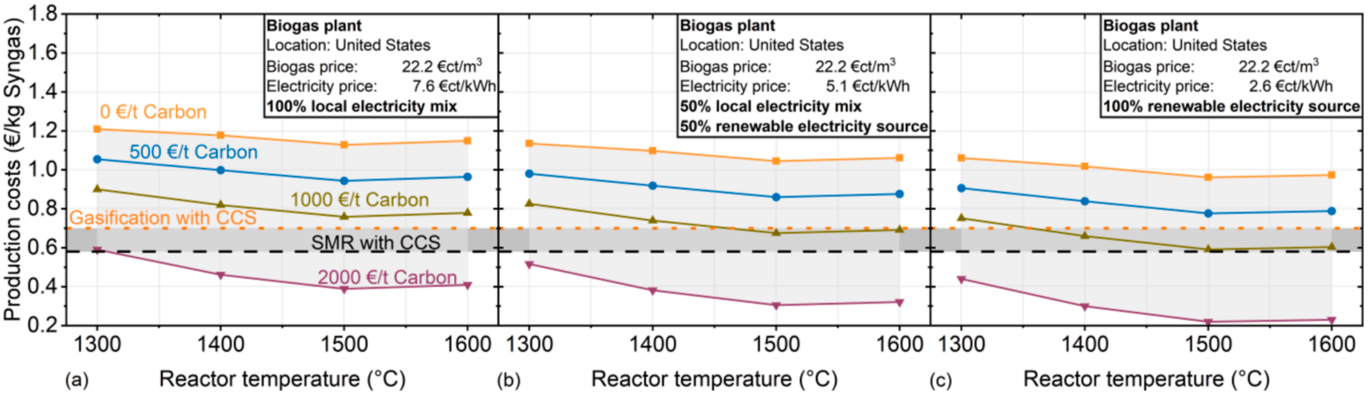

Fig. 12. Syngas production costs via thermal biogas pyrolysis in the United States as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average production costs for syngas via steam reforming and coal gasification (both with CCS) are shown as reference.

becomes negative, hereby enabling the process to serve as a CO_2 sink. In particular, for every kg of syngas produced, up to 0.4 kg of CO_2 (with 50 % renewable electricity sources and 50 % local electricity mix, Fig. 11b) or over 1 kg of CO_2 (with 100 % renewable electricity sources, Fig. 11c) can be removed from the environment. The huge potential to capture atmosphere-borne carbon makes the biogas pyrolysis process much more environmentally attractive than conventional processes, even if those are supplemented with CCS.

3.2.2. United States of America

Fig. 12 elucidates syngas production costs for thermal biogas pyrolysis in the United States as a function of the pyrolysis reactor temperature with variable sales prices for the produced carbon and for variable electricity sources. Local biogas prices, data on electricity sources and their respective costs as well as the corresponding CO_2 emissions of the power generation are taken from relevant literature [71,75–78]. Furthermore, corresponding production costs using steam reforming and coal gasification (both with CCS) for syngas production are shown as reference [49,92].

Due to low electricity costs and a large availability of biomass, which can be cheaply converted into biogas [75], syngas can be produced in a comparatively cost-effective way. The lowest production costs can be achieved at a reactor temperature of 1500 °C, regardless of the electricity price or carbon revenue. With a 100 % local electricity composition (Fig. 12a), the carbon produced during thermal pyrolysis must be sold for at least 1000 €/t in order to enable syngas production costs of less than 0.80 €/kg syngas. However, these costs are still higher compared to syngas production *via* gasification with CCS (0.70 €/kg syngas) and significantly higher than steam reforming with CCS (0.58 €/kg syngas). With the current electricity mix, the pyrolysis of biogas can hardly compete with conventional methods. Only an increasing share of renewable energies in the electricity supply, and therefore cheaper electricity in the United States, production costs of less than 0.70 €/kg syngas with a 50 % local electricity mix and 50 % electricity from renewable energies (Fig. 12b) or less than 0.60 €/kg syngas with 100 % electricity from renewable sources (Fig. 12c) can be achieved. Herein, carbon revenues of 1000 €/t are assumed. If the carbon is sold for only 500 €/t, conventional methods coupled with CCS cannot be beaten economically without any CO_2 taxation. Only with a theoretical carbon revenue of 2000 €/t, hypothetical syngas production prices of approx. 0.20 €/kg (with power from renewable sources only) may be possible, which would be far lower than production costs *via* conventional routes even without CCS.

In contrast, biogas pyrolysis is highly attractive with regard to ecologic aspects. Fig. 13 shows the resulting CO_2 sources and sinks due to electricity supply, H_2 dilution, CO_2 fixation by biomass as well as the total CO_2 balance for thermal biogas pyrolysis in the United States as a function of the reactor temperature and under consideration of different electricity sources. Data for syngas production *via* steam reforming and coal gasification (both with CCS) are shown as reference [92].

Compared to China (Fig. 11), the current local electricity production in the USA causes significantly lower greenhouse gas emissions, namely 0.364 kg CO_2e/kWh [78]. Therefore, the production of syngas *via* biogas pyrolysis represents a CO_2 sink already with the current electricity

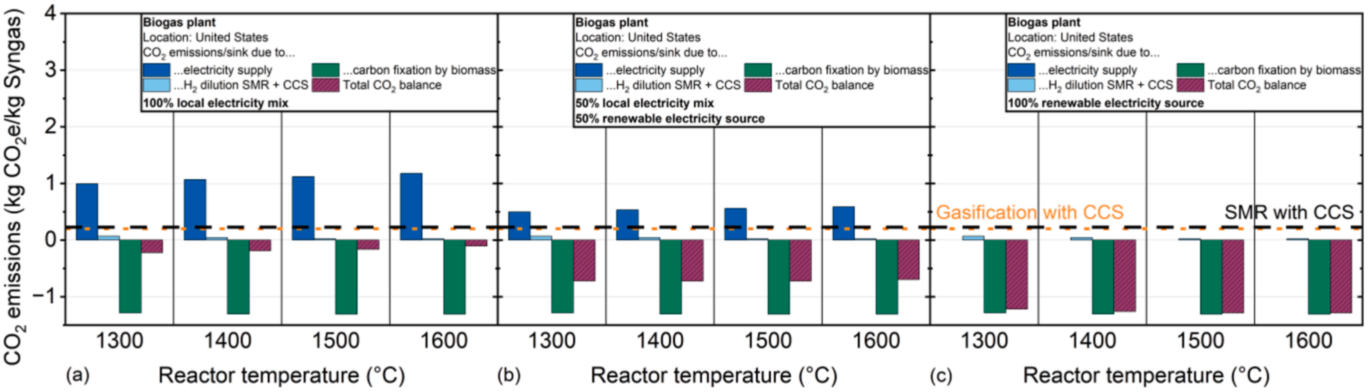

Fig. 13. CO_2 emissions via thermal biogas pyrolysis in the United States as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average CO_2 emissions for syngas production via steam reforming and coal gasification (both with CCS) are shown as reference.

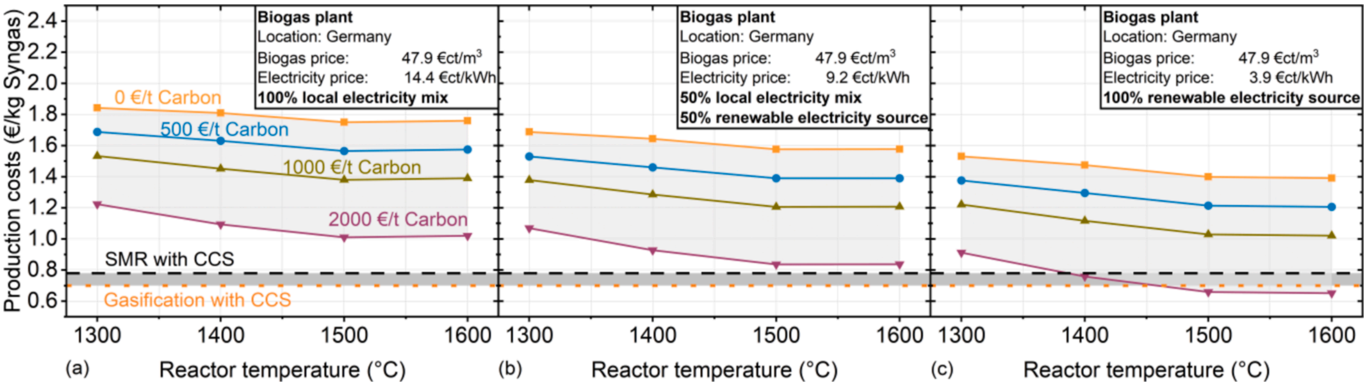

Fig. 14. Syngas production costs via thermal biogas pyrolysis in Germany as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average production costs for syngas via steam reforming and coal gasification (both with CCS) are shown as reference.

supply. In terms of CO_2 emissions, the process is always more environmentally friendly than conventional routes for all electricity compositions considered herein. While only around 0.1 to 0.2 kg CO_2/kg syngas can be removed from the environment with the current electricity mix (Fig. 13a), over 1 kg CO_2/kg syngas can be fixed with a completely emission-neutral electricity supply (Fig. 13c).

In summary, carbon capture using biogas pyrolysis can be realized in the USA already nowadays, but it is not yet economically viable. Only a CO_2-neutral and cheaper power supply or a high-quality utilization of the carbon can ensure a process that is both economically and ecologically feasible. Beyond these aspects, the different dimensions in production capacity between biogas utilization and conventional syngas production processes must be taken into account as well. These are discussed in the last section.

3.2.3. Germany

Fig. 14 reveals syngas production costs for thermal biogas pyrolysis in Germany as a function of the pyrolysis reactor temperature with

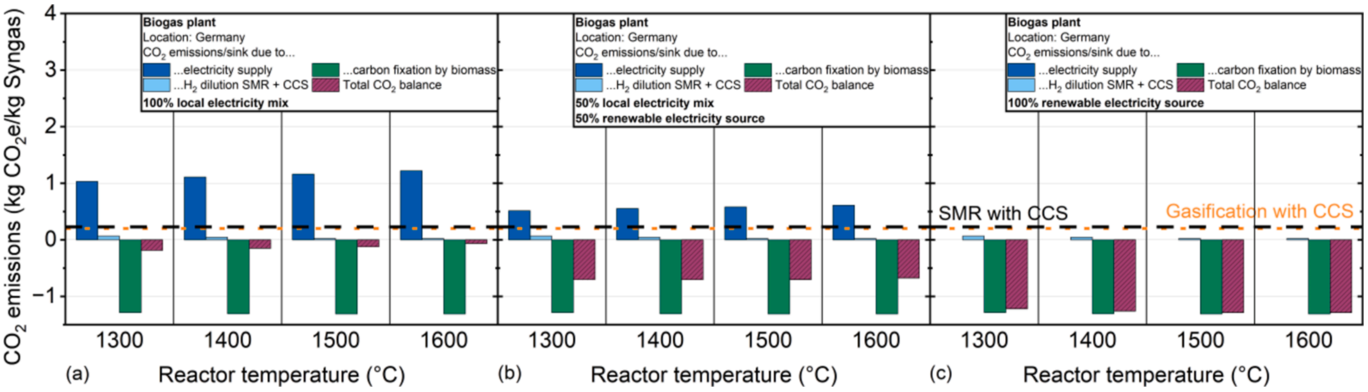

Fig. 15. CO_2 emissions via thermal biogas pyrolysis in Germany as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average CO_2 emissions for syngas production via steam reforming and coal gasification (both with CCS) are shown as reference.

variable sales prices for the produced carbon and for variable electricity sources. Local biogas prices, data for electricity sources and their respective costs as well as the corresponding CO_2 emissions of the power generation are taken from relevant literature [71,79–81]. In addition, corresponding production costs using steam reforming and coal gasification (both with CCS) for syngas production are shown as reference [49,92].

Even though Germany has considerable biomass potential [80], the current prices and costs for energy make it difficult to operate a potential biogas-to-syngas plant profitably. For instance, the syngas production costs for all electricity compositions considered herein are significantly higher than the costs *via* conventional production routes. Thermal pyrolysis can undercut syngas production costs from coal gasification and steam reforming (both with CCS) only if a carbon revenue of 2000 €/t and a power supply from 100 % renewable sources is assumed (Fig. 14c). For all other revenues, the syngas production costs *via* biogas pyrolysis are always between 1 and 2 €/kg syngas, which would still be more cost-intensive than conventional production routes, notably under some conditions even if a CO_2 taxation is added as ‘penalty’ to the conventional technologies and increases their production costs twofold [92].

Fig. 15 shows the CO_2 emissions and sinks caused by electricity supply, H_2 dilution, CO_2 fixation by biomass as well as the total CO_2 balance for thermal biogas pyrolysis in Germany as a function of the reactor temperature and with different electricity sources. Data for syngas production *via* steam reforming and coal gasification are shown as reference [92].

Since approx. 55 % of the current electricity supply in Germany already comes from renewable sources [81], biogas pyrolysis – similar to the situation in the USA – could immediately serve as a CO_2 sink with the current electricity supply (Fig. 15a): An overall negative CO_2 balance of −0.1 to −0.2 kg CO_2/kg syngas could be achieved. Compared to conventional syngas production routes (with CCS), the process is therefore lower in emissions and allows carbon to be effectively fixed. A further decarbonization of the power supply chain enables even better CO_2 balances. For instance, with an entirely emission-neutral power supply (Fig. 15c), over 1 kg CO_2/kg syngas can be fixed. Despite these excellent ecological prospective and despite the high national biomass potential, the production of syngas *via* biogas pyrolysis is currently not profitable in Germany. In this respect, the very high costs for energy [79], which also contribute to relatively high biogas production costs *via* fermentation, are the main obstacle. However, if the electricity price could be reduced to a considerable extent, i.e. by a further decarbonization of the electricity supply, the pyrolysis of biogas may be considered as a complementary technology for indirect carbon capture (fixing atmosphere-borne CO_2 in the form of solid carbon) with simultaneous syngas production. For the economically competitive large-scale production of syngas, supplementing conventional production technologies with CCS seem more feasible – at least, as long as CO_2 taxation is not taken into account.

3.2.4. Türkiye

With total collectible manure of more than 176 million tons, agricultural waste of more than 17 million tons, and a biogas potential of over 17 billion m^3 per year [85], Türkiye offers a large bio-based feedstock and therefore could be a particularly attractive location for biogas pyrolysis. Consequently, Fig. 16 illustrates syngas production costs for thermal biogas pyrolysis in Türkiye as a function of the pyrolysis reactor temperature with variable sales prices for the produced carbon and for variable electricity sources. Local biogas prices, data for electricity sources and their respective costs as well as the corresponding CO_2 emissions of the power generation are taken from relevant literature [71,83–85]. Moreover, syngas production costs using steam reforming and coal gasification (both with CCS) are shown as reference [49,92].

Due to the comparatively low biogas prices, a profitable biogas-to-syngas process could be established in Türkiye in principle. However, the to date relatively high electricity costs impede this: With the current electricity mix, only non-competitive syngas production costs between 1 €/kg (at 1000 €/t carbon) and 1.5 €/kg (at 0 €/t carbon) can be achieved by means of biogas pyrolysis (Fig. 16a). Since Türkiye is one of the countries with the highest potential for renewable energies in Europe and the Mediterranean region [99], a transformation of the electricity supply towards emission neutrality is predicted to allow for significantly lower electricity costs of less than 5 €ct/kWh [71]. Combined with the comparatively low costs for biogas production, syngas prices of less than 0.7 €/kg (for a carbon revenue of at least 1000 €/t) would be possible if the electricity is exclusively provided by renewable sources (Fig. 16c). While this would undercut the costs of conventional coal gasification with CCS, SMR with CCS would still remain the cheapest option; only if a carbon selling price of 2000 €/t is assumed, biogas pyrolysis becomes the most attractive option from an economic point of view.

Fig. 17 shows the CO_2 emissions and sinks related to electricity supply, H_2 dilution, CO_2 fixation by biomass as well as the total CO_2 balance for thermal biogas pyrolysis in Türkiye as a function of the reactor temperature and with different electricity sources. Data on syngas production *via* steam reforming and coal gasification are shown as reference [92].

With the current Turkish electricity mix (Fig. 17a), the production of syngas *via* pyrolysis of biogas exhibits net CO_2 emissions. These are almost completely caused by the electricity supply, which relies by almost 58 % on fossil sources, causing approx. 0.464 CO_2e/kWh [84]. Nevertheless, under all reactor operation temperatures considered herein, the overall carbon footprint is always advantageous compared to conventional production routes coupled with CCS that cause 0.2 to 0.24 kg CO_2/kg syngas. Assuming that the decarbonization of the electricity

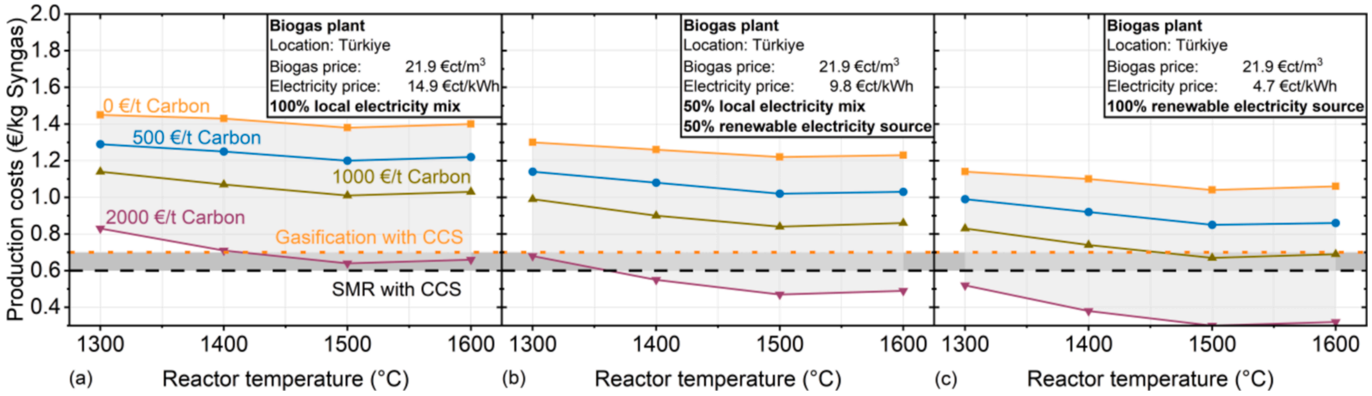

Fig. 16. Syngas production costs via thermal biogas pyrolysis in Türkiye as a function of pyrolysis reactor temperature with a variable carbon selling price and different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average production costs for syngas via steam reforming and coal gasification (both with CCS) are shown as reference.

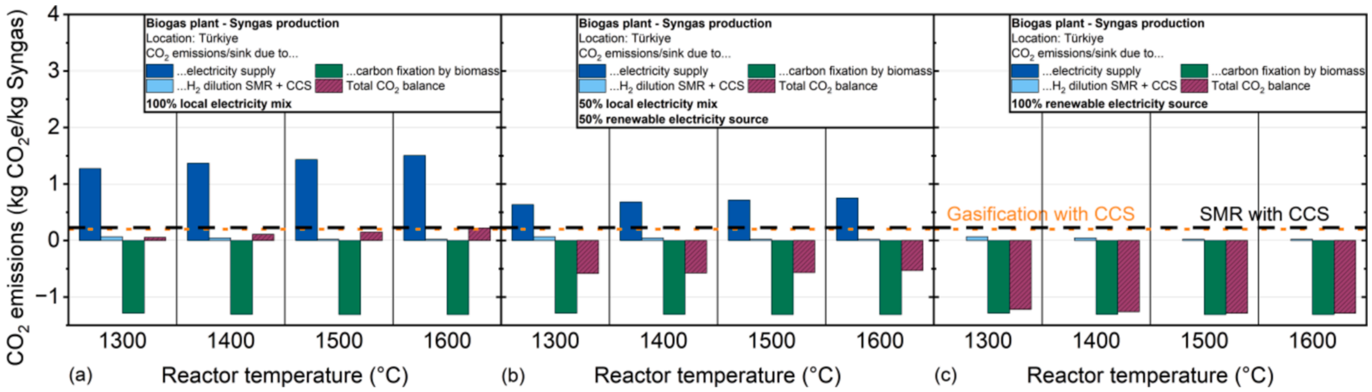

Fig. 17. CO_2 emissions via thermal biogas pyrolysis in Türkiye as a function of pyrolysis reactor temperature with different electricity sources: 100% local electricity mix (a), 50% local electricity mix and 50% renewable electricity sources (b), and 100% renewable electricity sources (c). Average CO_2 emissions for syngas production via steam reforming and coal gasification (both with CCS) are shown as reference.

Table 7

Costs for syngas production via biogas pyrolysis with a 100 % local electricity mix and a theoretical 100 % electricity supply from renewable sources at a reactor temperature of 1500 °C as well as a constant carbon selling price of 500 €/t and 1000 €/t. Data for syngas production costs via steam reforming and coal gasification (both with (w/) CCS) are shown as reference. GER: Germany; TUR: Türkiye.

Country	Minimum syngas production costs (€/kg syngas)			
	Pyrolysis		Conventional processes (w/ CCS)	
			Steam reforming	Coal gasification
	Local e-mix	Renewable electricity	Independent from e-mix	
Syngas production costs (€/kg syngas) at a carbon selling price of 500 €/t carbon				
China	0.84	0.67	0.68	0.70
USA	0.94	0.77	0.58	0.70
GER	1.56	1.21	0.78	0.70
TUR	1.20	0.85	0.60	0.70
Syngas production costs (€/kg syngas) at a carbon selling price of 1000 €/t carbon				
China	0.66	0.49	0.68	0.70
USA	0.75	0.59	0.58	0.70
GER	1.38	1.02	0.78	0.70
TUR	1.01	0.67	0.60	0.70

supply continues in the next years, biogas pyrolysis could be established as a bridge technology already today. Once a 100 % emission-free electricity supply is possible (Fig. 17c), a total of over 1 kg of CO_2 can be converted into solid carbon per kg of syngas produced. In summary, Türkiye is an in principle highly suitable location with a large potential for supply of sustainable biogas and power from renewable sources. In order to ensure competitiveness with coal gasification, the power supply must be decarbonized quickly to ensure feasible electricity costs and an overall negative CO_2 balance. Despite the slightly lower costs of syngas production by means of SMR with CCS, ecological considerations or CO_2 taxation may promote the attractiveness of biogas pyrolysis in the future.

3.2.5. *Summary*

Table 7 shows the syngas production costs *via* biogas pyrolysis under the assumption of the respective current local electricity mix and entirely renewable electricity sources, as well as *via* steam reforming and coal gasification (both with CCS) for each country considered herein. A carbon selling price of 500 €/t and 1000 €/t is compared, as these price levels are expected to be realistic. Furthermore, production costs are given at a constant reactor temperature of 1500 °C for all locations. At this temperature and with an initial CH_4:CO_2 ratio of 1:1 in the biogas, full conversion of CH_4 and CO_2 along with an H_2:CO ratio of 2:1 in the effluent gas stream can be realized, which leads to minimum syngas production costs, irrespective of location and for all carbon selling prices. Note, that as already discussed in the previous sections, it was assumed that the syngas production costs *via* steam reforming and coal gasification are independent of the electricity mix, as the reactor commonly is heated by autothermal combustion [92].

If a carbon selling price of 500 €/t is considered, the biogas-to-syngas process is currently unable to compete with the price of conventional production routes with CCS and without CO_2 taxes in any country. Among the countries evaluated in this study, sustainable syngas would be most expensive in Germany (1.56 €/kg and 1.38 €/kg assuming a carbon revenue of 500 €/t and 1000 €/t, respectively). If electricity is generated exclusively from renewable sources, prices close to conventional production routes with CCS can be achieved in China, the USA, and Türkiye, even without CO_2 taxation (which also needs to be considered even when using CCS) [92]. Moreover, China, the USA, and Türkiye show the lowest costs of 0.67 €/kg, 0.77 €/kg, and 0.85 €/kg, respectively. While in Germany the biogas-based process (at 1.21 €/kg

Table 8

Emissions for syngas production via biogas pyrolysis at a reactor temperature of 1500 °C with a 100 % local electricity mix and a theoretical 100 % electricity supply from renewable sources. Data for syngas production costs via steam reforming and coal gasification (both with (w/) CCS) are shown as reference. GER: Germany; TUR: Türkiye.

Country	Emissions (kg CO_2e/kg syngas)			
	Pyrolysis		Conventional processes (w/ CCS)	
			Steam reforming	Coal gasification
	Local e-mix	Renewable electricity	Independent from e-mix	
China	0.51 (1500 °C)	−1.28 (1500 °C)	0.24	0.20
USA	−0.16 (1500 °C)	−1.28 (1500 °C)	0.24	0.20
GER	−0.12 (1500 °C)	−1.28 (1500 °C)	0.24	0.20
TUR	0.14 (1500 °C)	−1.28 (1500 °C)	0.24	0.20

syngas) could only compete with conventional routes if CO_2 taxation is considered, China, the USA, and Türkiye are feasible locations for cost-effective syngas production *via* biogas pyrolysis already now or in the foreseeable future.

Biogas pyrolysis becomes even more advantageous if a carbon selling price of 1000 €/t and electricity supply from renewable sources is assumed: The syngas prices of 0.59 €/kg in the USA and of 0.67 €/kg in Türkiye allow to undercut the coal gasification process with CCS (0.70 €/kg syngas). In China, thermal pyrolysis enables syngas prices as low as 0.49 €/kg, which is economically even more viable than steam reforming with CCS (0.68 €/kg syngas). For all other cases, steam reforming with CCS remains the cheapest option. However, this may change if CO_2 taxation is introduced, which would emphasize ecological aspects that are discussed next.

Table 8 shows the emissions caused by the biogas pyrolysis process, either with a 100 % local electricity mix or with electricity from 100 % renewable sources, as well as *via* steam reforming and coal gasification (both with CCS). Herein, analogous to the data depicted in Table 7, a reactor temperature of 1500 °C was assumed for all locations.

Except China, using the current electricity mix would allow for syngas production *via* thermal pyrolysis in a more environmentally friendly than if conventional production routes with CCS are chosen. As emissions during electricity generation in the USA and Germany are comparably low already nowadays, the establishment of biogas pyrolysis reactors as suggested in this study would enable immediate net-negative emissions: In terms of CO_2-equivalents, -0.12 kg CO_2e/kg syngas and -0.16 kg CO_2e/kg syngas can be achieved in Germany and the USA, respectively. Although negative CO_2 balances are not yet achievable in Türkiye, the pyrolysis-related emissions are still lower than those caused by steam reforming or coal gasification with CCS. The high emissions caused during electricity generation impede an ecological operation of thermal biogas pyrolysis processes in China to date. However, if electricity is supplied exclusively from renewable sources, a net-negative CO_2 balance of -1.28 kg CO_2e/kg syngas is theoretically possible in all locations, which strongly underscores the ecological attractiveness of the biogas-to-syngas process as an overall CO_2 sink.

In conclusion, thermal biogas pyrolysis can represent a potential alternative syngas production route in China, the USA, and in Türkiye. Assuming an electricity supply from renewable sources in all three countries, the pyrolysis process can compete economically with conventional production routes with CCS, even if CO_2 taxation remains unconsidered. From an ecological point of view, net-negative emissions of up to -1.28 CO_2/kg syngas can be achieved in all countries. Notably, the USA are the only location where biogas pyrolysis could be conducted with both, economic and ecological advantages over conventional technologies already nowadays with the current electricity mix.

In addition, it must also be taken into account that potential biogas-to-syngas plants would have a significantly lower production capacity compared to coal gasification plants, because fermentation plants for biogas production are limited in their capacity. Herein, a maximum biogas production rate of 2000 m^3/h is usually assumed, as the costs for transporting the biomass to the fermentation plant can no longer be compensated for at higher capacities [58]. A complete conversion to syngas would provide an annual production capacity of approx. 26 million m^3, which is only a fraction of commercial steam reforming or coal gasification plants that can have a capacity of over 1 billion m^3 syngas per year [100,101]. As a result, biogas-to-syngas plants must be constructed and operated in a decentralized manner, preferably directly at the biogas source, to ensure that all excess biomass is utilized properly.

4. Conclusions

Within this work, a techno-economic assessment of thermal pyrolysis was conducted with a focus on two processes: the production of hydrogen from natural gas and the production of syngas from biogas. Pyrolytic hydrogen production was compared with conventional production routes, namely steam reforming of methane and electrolysis, and pyrolytic syngas production was compared with steam reforming of methane and coal gasification. In particular, production costs and carbon footprint were evaluated under consideration of different pyrolysis reactor temperatures and carbon selling prices as well as location-dependent external parameters, i.e., costs for natural gas, biogas, and electricity sources, as well as corresponding greenhouse gas emissions. For this purpose, a process was simulated for both production routes using Aspen Plus; experimental data obtained during previous studies from a lab-scale pyrolysis reactor operated under industrially relevant conditions served as input parameters for the simulations [6,8,25]. China, the United States of America (USA), Germany, Saudi Arabia, and Türkiye were studied as potential locations.

Costs for hydrogen production *via* natural gas pyrolysis are generally similar or even lower compared to steam reforming, if a carbon selling price of 500 €/kg is assumed. If the costs for natural gas and electricity are low, such as in the USA and in Saudi Arabia, H_2 production costs of less than 1 €/kg can be achieved. Although electrolysis is the only entirely emission-free production pathway, it requires much more energy than pyrolysis (herein, a value of 50 kWh/kg H_2 was assumed for electrolysis, and a demand of approx. 5.3 kWh/kg H_2 was calculated for thermal pyrolysis at 1200 °C), resulting in substantially higher H_2 production costs. The latter process has the advantage of potentially being operated completely emission-free, however, this requires a power supply that solely relies on renewable sources. For instance, with the current electricity supply in Saudi Arabia, thermal pyrolysis releases approx. 3 times less CO_2e per kg H_2 compared to electrolysis. Although even in the most favorable case with a power supply from 100 % renewable sources natural gas pyrolysis generates inevitable emissions of more than 1 kg CO_2/ kg H_2 that are caused by natural gas extraction, pyrolysis is ecologically still much more favorable compared to steam reforming, which causes 8.47 kg CO_2e/kg H_2 without CCS and 2.10 kg CO_2e/kg H_2 with CCS.

Overall, local factors greatly govern the economic and ecologic appeal of pyrolysis processes. In countries with comparably low electricity costs and moderate natural gas prices, such as the USA or China, natural gas pyrolysis is a suitable bridging technology, as it can already nowadays supply significantly cheaper and lower-emission hydrogen compared to electrolysis with the current electricity supply. While hydrogen from pyrolysis is significantly cheaper than H_2 from electrolysis and steam reforming with CCS in the USA even with a decarbonized electricity supply, electrolysis is the cheapest H_2 production method in China in the long term. In Germany, both pyrolysis and electrolysis are more cost-intensive than steam reforming with CCS, whereby electrolysis appears to be the more feasible alternative in the long term due to the small cost difference and the advantageous CO_2 footprint compared to pyrolysis.

The results discussed above consider carbon selling prices between 500 €/t and 1000 €/t, which are assumed to be realistic in the short-term under consideration of the properties of pyrolytic carbon that were reported previously [6,25]. A more specialized application of carbon, e.g., as activated carbon, could increase the carbon selling price and consequently decrease hydrogen production costs even further; for instance, a carbon selling price of 2000 €/t carbon would theoretically lead to negative H_2 production costs. However, the characterization and identification of possible fields of application for the accruing carbon is still subject to current research [39]. Furthermore, it is important to mention that the carbon market is currently much smaller than the hydrogen market [39]. Hence, meeting the entire global demand for hydrogen solely *via* natural gas pyrolysis seems unrealistic, simply because way too much carbon would be produced. In some regions, however, it could be a reasonable production technology that enables the production of hydrogen that is, compared to alternative production routes, significantly cheaper and lower in emissions.

Biogas, on the other hand, is currently mainly used to generate electricity. Although its (large-scale) utilization as a feedstock for the production of renewable syngas is still under investigation, biogas pyrolysis is of great ecological potential since the process can serve as a CO_2 sink that enables negative emissions of up to −1.28 kg CO_2e/kg syngas. From an economic point of view, the syngas production costs can compete with those of conventional syngas production methods (with CCS) in the USA, Türkiye, and Germany. In China, where minimum syngas production costs of 0.49 €/kg at a carbon selling price of 1000 €/t can be achieved, the biogas pyrolysis process can outperform steam reforming and coal gasification with CCS even economically – notably, although CO_2 taxation remains unconsidered throughout this work. To ensure such low syngas production costs combined with negative CO_2 emissions, electricity needs to be supplied completely from renewable sources.

In conclusion, biogas pyrolysis should be exploited at locations where a significant amount of biomass is produced or where material recycling seems economically and ecologically more feasible than simple power generation. However, it must be taken into account that fermentation plants for biogas production are limited in their production capacity, meaning that production must be decentralized for large-scale syngas production. In addition, the biomass potential is typically insufficient to cover the entire syngas demand. To date, these aspects make the biogas-to-syngas process particularly interesting as a complementary technology for carbon capture while at the same time renewable syngas is produced.

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CRediT authorship contribution statement

Ahmet Çelik: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Iadh Ben Othman:** Investigation, Formal analysis. **Yannik Neudeck:** Investigation, Formal analysis. **Olaf Deutschmann:** Supervision, Resources, Project administration, Conceptualization. **Patrick Lott:** Writing – original draft, Validation, Supervision, Resources, Project administration, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.enconman.2024.119414.

Data availability

All data that were used throughout this study are listed in tables, figures, and the electronic supporting information.

References

[1] Sánchez-Bastardo N, Schlögl R, Ruland H. Methane pyrolysis for zero-emission hydrogen production: A potential bridge technology from fossil fuels to a renewable and sustainable hydrogen economy. Ind Eng Chem Res 2021;60:11855–81. https://doi.org/10.1021/acs.iecr.1c01679.

[2] Machhammer O, Bode A, Hormuth W. Financial and ecological evaluation of hydrogen production processes on large scale. Chem Eng Technol 2016;39:1185–93. https://doi.org/10.1002/ceat.201600023.

[3] Muradov N, Veziroğlu T. From hydrocarbon to hydrogen–carbon to hydrogen economy. Int J Hydrogen Energy 2005;30:225–37. https://doi.org/10.1016/j.ijhydene.2004.03.033.

[4] Ashik UPM, Wan Daud WMA, Abbas HF. Production of greenhouse gas free hydrogen by thermocatalytic decomposition of methane – A review. Renewable and Sustainable Energy Rev 2015;44:221–56. https://doi.org/10.1016/j.rser.2014.12.025.

[5] Ehrhardt K, Scheiff F, Flick D, Lott P, Mokashi M, Heitlinger H, et al. Pyrolysis of methane: interplay between industrial design considerations and detailed chemistry evaluation. 13th European Congress of. Chem Eng 2021.

[6] Çelik A, Ben Othman I, Müller H, Lott P, Deutschmann O. Pyrolysis of biogas for carbon capture and carbon dioxide-free production of hydrogen. React Chem Eng 2024;9:108–18. https://doi.org/10.1039/d3re00360d.

[7] Raza A, Gholami R, Rezaee R, Rasouli V, Rabiei M. Significant aspects of carbon capture and storage – A review. Petroleum 2019;5:335–40. https://doi.org/10.1016/j.petlm.2018.12.007.

[8] Lott P, Mokashi MB, Müller H, Heitlinger DJ, Lichtenberg S, Shirsath AB, Janzer C, Tischer S, Maier L, Deutschmann O. Hydrogen production and carbon capture by gas phase methane pyrolysis: A feasibility study. ChemSusChem 2023;16:e202201720. https://doi.org/10.1002/cssc.202201720.

[9] Mokashi M, Shirsath AB, Lott P, Müller H, Tischer S, Maier L, et al. Understanding of gas-phase methane pyrolysis towards hydrogen and solid carbon with detailed kinetic simulations and experiments. Chem Eng J 2024;479:147556. https://doi.org/10.1016/j.cej.2023.147556.

[10] Keipi T, Tolvanen KES, Tolvanen H, Konttinen J. Thermo-catalytic decomposition of methane: The effect of reaction parameters on process design and the utilization possibilities of the produced carbon. Energy Convers Manage 2016;126:923–34. https://doi.org/10.1016/j.enconman.2016.08.060.

[11] Çelik A, Ben Othman I, Müller H, Deutschmann O, Lott P. CO_2-free production of hydrogen via pyrolysis of natural gas: influence of non-methane hydrocarbons on product composition, methane conversion, hydrogen yield, and carbon capture. Discover Chem Eng 2024;4:29. https://doi.org/10.1007/s43938-024-00067-4.

[12] Sharif Zein SH, Mohamed AR, Talpa Sai PS. Kinetic studies on catalytic decomposition of methane to hydrogen and carbon over Ni/TiO_2 catalyst. Ind Eng Chem Res 2004;43:4864–70. https://doi.org/10.1021/ie034208f.

[13] Muradov N. CO_2-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuel. Energy Fuels 1998;12:41–8. https://doi.org/10.1021/ef9701145.

[14] Muradov N. Catalysis of methane decomposition over elemental carbon. Catal Commun 2001;2:89–94. https://doi.org/10.1016/s1566-7367(01)00013-9.

[15] Serrano DP, Botas JA, Guil-Lopez R. H_2 production from methane pyrolysis over commercial carbon catalysts: Kinetic and deactivation study. Int J Hydrogen Energy 2009;34:4488–94. https://doi.org/10.1016/j.ijhydene.2008.07.079.

[16] Abánades A, Ruiz E, Ferruelo EM, Hernández F, Cabanillas A, Martínez-Val JM, et al. Experimental analysis of direct thermal methane cracking. Int J Hydrogen Energy 2011;36:12877–86. https://doi.org/10.1016/j.ijhydene.2011.07.081.

[17] Muradov N, Smith F, Huang C, T-Raissi A. Autothermal catalytic pyrolysis of methane as a new route to hydrogen production with reduced CO_2 emissions. Catal Today 2006;116:281–8. https://doi.org/10.1016/j.cattod.2006.05.070.

[18] Shilapuram V, Ozalp N, Oschatz M, Borchardt L, Kaskel S. Hydrogen production from catalytic decomposition of methane over ordered mesoporous carbons (CMK-3) and carbide-derived carbon (DUT-19). Carbon 2014;67:377–89. https://doi.org/10.1016/j.carbon.2013.10.008.

[19] Kerscher F, Stary A, Gleis S, Ulrich A, Klein H, Spliethoff H. Low-carbon hydrogen production via electron beam plasma methane pyrolysis: Techno-economic analysis and carbon footprint assessment. Int J Hydrogen Energy 2021;46:19897–912. https://doi.org/10.1016/j.ijhydene.2021.03.114.

[20] Fulcheri L, Probst N, Flamant G, Fabry F, Grivei E, Bourrat X. Plasma processing: a step towards the production of new grades of carbon black. Carbon 2002;40:169–76. https://doi.org/10.1016/s0008-6223(01)00169-5.

[21] Geißler T, Plevan M, Abánades A, Heinzel A, Mehravaran K, Rathnam RK, et al. Experimental investigation and thermo-chemical modeling of methane pyrolysis in a liquid metal bubble column reactor with a packed bed. Int J Hydrogen Energy 2015;40:14134–46. https://doi.org/10.1016/j.ijhydene.2015.08.102.

[22] Kang D, Rahimi N, Gordon MJ, Metiu H, McFarland EW. Catalytic methane pyrolysis in molten $MnCl_2$-KCl. Appl Catal, B 2019;254:659–66. https://doi.org/10.1016/j.apcatb.2019.05.026.

[23] Dadsetan M, Khan MF, Salakhi M, Bobicki ER, Thomson MJ. CO_2-free hydrogen production via microwave-driven methane pyrolysis. Int J Hydrogen Energy 2023;48:14565–76. https://doi.org/10.1016/j.ijhydene.2022.12.353.

[24] Muradov N. Hydrogen via methane decomposition: An application for decarbonization of fossil fuels. Int J Hydrogen Energy 2001;26:1165–75. https://doi.org/10.1016/s0360-3199(01)00073-8.

[25] Mokashi M, Shirsath AB, Çelik A, Lott P, Müller H, Tischer S, et al. Methane pyrolysis in packed bed reactors: Kinetic modeling, numerical simulations, and experimental insights. Chem Eng J 2024;485:149684. https://doi.org/10.1016/j.cej.2024.149684.

[26] Shirsath AB, Mokashi M, Lott P, Müller H, Pashminehazar R, Sheppard T, et al. Soot formation in methane pyrolysis reactor: Modeling soot growth and particle characterization. J Phys Chem A 2023;127:2136–47. https://doi.org/10.1021/acs.jpca.2c06878.

[27] Appel J, Bockhorn H, Frenklach M. Kinetic modeling of soot formation with detailed chemistry and physics: laminar premixed flames of C_2 hydrocarbons. Combust Flame 2000;121:122–36. https://doi.org/10.1016/s0010-2180(99)00135-2.

[28] Frenklach M. Reaction mechanism of soot formation in flames. Phys Chem Chem Phys 2002;4:2028–37. https://doi.org/10.1039/b110045a.

[29] Norinaga K, Deutschmann O. Detailed kinetic modeling of gas-phase reactions in the chemical vapor deposition of carbon from light hydrocarbons. Ind Eng Chem Res 2007;46:3547–57. https://doi.org/10.1021/ie061207p.

[30] Norinaga K, Deutschmann O, Saegusa N, Hayashi J-I. Analysis of pyrolysis products from light hydrocarbons and kinetic modeling for growth of polycyclic aromatic hydrocarbons with detailed chemistry. J Anal Appl Pyrolysis 2009;86:148–60. https://doi.org/10.1016/j.jaap.2009.05.001.

[31] Norinaga K, Janardhanan VM, Deutschmann O. Detailed chemical kinetic modeling of pyrolysis of ethylene, acetylene, and propylene at 1073–1373 K with a plug-flow reactor model. Int J Chem Kinet 2008;40:199–208. https://doi.org/10.1002/kin.20302.

[32] Billaud F, Gueret C, Weill J. Thermal decomposition of pure methane at 1263 K. Experiments and mechanistic modelling Thermocim Acta 1992;211:303–22. https://doi.org/10.1016/0040-6031(92)87029-a.

[33] Matheu DM, Dean AM, Grenda JM, Green WH. Mechanism Generation with Integrated Pressure Dependence: A New Model for Methane Pyrolysis. J Phys Chem A 2003;107:8552–65. https://doi.org/10.1021/jp0345957.

[34] Arcos JMM, Santos DMF. The Hydrogen Color Spectrum: Techno-Economic Analysis of the Available Technologies for Hydrogen Production. Gases 2023;3:25–46. https://doi.org/10.3390/gases3010002.

[35] Parkinson B, Tabatabaei M, Upham DC, Ballinger B, Greig C, Smart S, et al. Hydrogen production using methane: Techno-economics of decarbonizing fuels and chemicals. Int J Hydrogen Energy 2018;43:2540–55. https://doi.org/10.1016/j.ijhydene.2017.12.081.

[36] Parkinson B, Balcombe P, Speirs JF, Hawkes AD, Hellgardt K. Levelized cost of CO_2 mitigation from hydrogen production routes. Energy Environ Sci 2019;12:19–40. https://doi.org/10.1039/c8ee02079e.

[37] Timmerberg S, Kaltschmitt M, Finkbeiner M. Hydrogen and hydrogen-derived fuels through methane decomposition of natural gas – GHG emissions and costs. Energy Convers Manage: X 2020;7:100043. https://doi.org/10.1016/j.ecmx.2020.100043.

[38] Keipi T, Tolvanen H, Konttinen J. Economic analysis of hydrogen production by methane thermal decomposition: Comparison to competing technologies. Energy Convers Manage 2018;159:264–73. https://doi.org/10.1016/j.enconman.2017.12.063.

[39] Muradov NZ, Veziroğlu TN. “Green” path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies. Int J Hydrogen Energy 2008;33:6804–39. https://doi.org/10.1016/j.ijhydene.2008.08.054.

[40] Böttcher A, Hennrich F, Rösner H, Malik S, Kappes MM, Lichtenberg S, et al. Growth of novel carbon phases by methane infiltration of free-standing single-walled carbon nanotube films. Carbon 2007;45:1085–96. https://doi.org/10.1016/j.carbon.2006.12.008.

[41] Michelsen HA, Colket MB, Bengtsson P-E, D’Anna A, Desgroux P, Haynes BS, et al. A review of terminology used to describe soot formation and evolution under combustion and pyrolytic conditions. ACS Nano 2020;14:12470–90. https://doi.org/10.1021/acsnano.0c06226.

[42] Prabowo J, Lai L, Chivers B, Burke D, Dinh AH, Ye L, et al. Solid carbon co-products from hydrogen production by methane pyrolysis: Current understandings and recent progress. Carbon 2024;216:118507. https://doi.org/10.1016/j.carbon.2023.118507.

[43] Ji Y, Palmer C, Foley EE, Giovine R, Yoshida E, Sebti E, et al. Valorizing the carbon byproduct of methane pyrolysis in batteries. Carbon 2023;204:26–35. https://doi.org/10.1016/j.carbon.2022.12.044.

[44] Fan Y, Fowler GD, Zhao M. The past, present and future of carbon black as a rubber reinforcing filler – A review. J Cleaner Prod 2020;247:119115. https://doi.org/10.1016/j.jclepro.2019.119115.

[45] Lockwood FC, van Niekerk JE. Parametric study of a carbon black oil furnace. Combust Flame 1995;103:76–90. https://doi.org/10.1016/0010-2180(95)00053-9.

[46] Johnson PH, Cooper WT, Forseth GJ. Large particle oil furnace black. A new type of carbon black. Rubber Chem Technol 1972;45:145–59. https://doi.org/10.5254/1.3544694.

[47] Wu S, Wang Z, Guo S, Cai Y, Zhang J, Huangfu C, et al. Life-cycle-based reconfiguration of sustainable carbon black production: Integrated conventional technique with waste tire pyrolysis and its future improvement potentials. J Cleaner Prod 2024;442:141022. https://doi.org/10.1016/j.jclepro.2024.141022.

[48] Howarth RW, Jacobson MZ. How green is blue hydrogen? Energy Sci Eng 2021;9:1676–87. https://doi.org/10.1002/ese3.956.

[49] Katebah M, Mm A-R, Linke P. Analysis of hydrogen production costs in Steam-Methane Reforming considering integration with electrolysis and CO_2 capture. Clean. Eng Technol 2022;10:100552. https://doi.org/10.1016/j.clet.2022.100552.

[50] Luk HT, Mondelli C, Ferré DC, Stewart JA, Pérez-Ramírez J. Status and prospects in higher alcohols synthesis from syngas. Chem Soc Rev 2017;46:1358–426. https://doi.org/10.1039/c6cs00324a.

[51] Nevzorova T, Kutcherov V. Barriers to the wider implementation of biogas as a source of energy: A state-of-the-art review. Energ Strat Rev 2019;26:100414. https://doi.org/10.1016/j.esr.2019.100414.

[52] AspenTech (2024), Aspen Plus V12, https://www.aspentech.com/en/academic-program (25 September 2024).

[53] Gupta R, Bhardwaj KN, Choudhary C, Chandna P, Jain KK, Kaur A, et al. Biofuels: The Environment-Friendly Energy Carriers. In: Kuhad RC, Singh A, editors. Biotechnology for Environmental Management and Resource Recovery. India: Springer India; 2013. p. 125–48. https://doi.org/10.1007/978-81-322-0876-1_8.

[54] Calbry-Muzyka A, Madi H, Rüsch-Pfund F, Gandiglio M, Biollaz S. Biogas composition from agricultural sources and organic fraction of municipal solid waste. Renew Energy 2022;181:1000–7. https://doi.org/10.1016/j.renene.2021.09.100.

[55] Guéret C, Daroux M, Billaud F. Methane pyrolysis: Thermodynamics. Chem Eng Sci 1997;52:815–27. https://doi.org/10.1016/s0009-2509(96)00444-7.

[56] Becker A, Hu Z, Hüttinger KJ. A hydrogen inhibition model of carbon deposition from light hydrocarbons. Fuel 2000;79:1573–80. https://doi.org/10.1016/s0016-2361(00)00030-2.

[57] Parkinson B, Matthews JW, McConnaughy TB, Upham DC, McFarland EW. Techno-Economic Analysis of Methane Pyrolysis in Molten Metals: Decarbonizing Natural Gas. Chem Eng Technol 2017;40:1022–30. https://doi.org/10.1002/ceat.201600414.

[58] Urban W, Girod K, Lohmann H, Dachs G, Zach C. Technologien und Kosten der Biogasaufbereitung und Einspeisung in das ErdgasnetzFraunhofer UMSICHT; 2009.

[59] Rafiee A, Khalilpour KR, Prest J, Skryabin I. Biogas as an energy vector. Biomass Bioenergy 2021;144:105935. https://doi.org/10.1016/j.biombioe.2020.105935.

[60] Leal Pérez BJ, Medrano Jiménez JA, Bhardwaj R, Goetheer E, van Sint AM, Gallucci F. Methane pyrolysis in a molten gallium bubble column reactor for sustainable hydrogen production: Proof of concept & techno-economic assessment. Int J Hydrogen Energy 2021;46:4917–35. https://doi.org/10.1016/j.ijhydene.2020.11.079.

[61] Hoffman Z. “Simulation and economic evaluation of coal gasification with SETS reforming process for power production. LSU Master’s Theses 2005. https://doi.org/10.31390/gradschool_theses.2269.

[62] Cheon S, Byun M, Lim D, Lee H, Lim H. Parametric Study for Thermal and Catalytic Methane Pyrolysis for Hydrogen Production: Techno-Economic and Scenario Analysis. Energies 2021;14:6102. https://doi.org/10.3390/en14196102.

[63] Roetzel W, Spang B. Berechnung von Wärmeübertragern. In: VDI-Wärmeatlas: Berechnungsblätter für den Wärmeübergang. Berlin, Heidelberg: Springer Berlin Heidelberg; 2002. p. 40–106. https://doi.org/10.1007/978-3-662-10743-0_3.

[64] Bhaskar A, Assadi M, Somehsaraei HN. Can methane pyrolysis based hydrogen production lead to the decarbonisation of iron and steel industry? Energy Convers Manage: X 2021;10:100079. https://doi.org/10.1016/j.ecmx.2021.100079.

[65] Thilakaratne R, Brown T, Li Y, Hu G, Brown R. Mild catalytic pyrolysis of biomass for production of transportation fuels: a techno-economic analysis. Green Chem 2014;16:627–36. https://doi.org/10.1039/C3GC41314D.

[66] Von Wald GA, Masnadi MS, Upham DC, Brandt AR. Optimization-based technoeconomic analysis of molten-media methane pyrolysis for reducing industrial sector CO_2 emissions. Sustainable Energy Fuels 2020;4:4598–613. https://doi.org/10.1039/D0SE00427H.

[67] Towler G, Sinnott R. Chapter 7 - Capital cost estimating. In: Towler G, Sinnott R, editors. Chemical Engineering Design. Third Edition. Butterworth-Heinemann; 2022. p. 307–54. https://doi.org/10.1016/B978-0-12-821179-3.00007-8.

[68] Franc-Dąbrowska J, Mądra-Sawicka M, Milewska A. Energy Sector Risk and Cost of Capital Assessment — Companies and Investors Perspective. Energies 2021;14:1613. https://doi.org/10.3390/en14061613.

[69] Towler G, Sinnott R. Chapter 2 - Process flowsheet development. In: Towler G, Sinnott R, editors. Chemical Engineering Design. Third Edition. Butterworth-Heinemann; 2022. p. 25–78. https://doi.org/10.1016/B978-0-12-821179-3.00002-9.

[70] Yang Z, Liang J. The environmental and economic impacts of phasing out cross-subsidy in electricity prices: Evidence from China. Energy 2023;284:129154. https://doi.org/10.1016/j.energy.2023.129154.

[71] International Renewable Energy Agency (2023), *Renewable power generation costs in 2022,* https://www.irena.org/Publications/2023/Aug/Renewable-Power-Generation-Costs-in-2022 (1 January 2024).

[72] Li X, Gao J, You S, Zheng Y, Zhang Y, Du Q, et al. Optimal design and techno-economic analysis of renewable-based multi-carrier energy systems for industries: A case study of a food factory in China. Energy 2022;244:123174. https://doi.org/10.1016/j.energy.2022.123174.

[73] Song Z, Zhang C, Yang G, Feng Y, Ren G, Han X. Comparison of biogas development from households and medium and large-scale biogas plants in rural China. Renewable and Sustainable Energy Rev 2014;33:204–13. https://doi.org/10.1016/j.rser.2014.01.084.

[74] EMBER Climate (2024), *China Electricity Review*, https://ember-climate.org/countries-and-regions/countries/china/ (23 August 2024).

[75] Erickson ED, Tominac PA, Zavala VM. Biogas production in United States dairy farms incentivized by electricity policy changes. Nat Sustain 2023;6:438–46. https://doi.org/10.1038/s41893-022-01038-9.

[76] International Renewable Energy Agency (2017), *Biogas Cost Reductions to Boost Sustainable Transport,* https://www.irena.org/news/articles/2017/Mar/Biogas-Cost-Reductions-to-Boost-Sustainable-Transport#:~:text=Typically%20the%20price%20of%20producing,industrial%20waste%2Dbased%20biogas%20production (23 August 2024).

[77] U.S. Energy Information Administration (2024), *Monthly Energy Review (March 2024),* www.eia.gov/mer (1 March 2024).

[78] EMBER Climate (2024), *United States Electricity Review*, https://ember-climate.org/countries-and-regions/countries/united-states-of-america/ (23 August 2024).

[79] Statistisches Bundesamt (Federal Office of Statistics) (2024), *Average prices for natural gas and electricity*, https://www.destatis.de/DE/Themen/Wirtschaft/Preise/Erdgas-Strom-DurchschnittsPreise/_inhalt.html#_ubhlkhr59 (23 August 2024).

[80] Fachagentur Nachwachsende Rohstoffe (supported by Federal Ministry of Food and Agriculture) (2020), *Bioenergy in Germany Facts and Figures*, https://www.fnr.de/fileadmin/allgemein/pdf/broschueren/broschuere_basisdaten_bioenergie_2020_engl_web.pdf (23 August 2024).

[81] EMBER Climate (2024), *Germany Electricity Review*, https://ember-climate.org/countries-and-regions/countries/germany/ (23 August 2024).

[82] Yahya SA, Iqbal T, Omar MM, Ahmad M. Techno-Economic Analysis of Fast Pyrolysis of Date Palm Waste for Adoption in Saudi Arabia. Energies 2021;14:6048. https://doi.org/10.3390/en14196048.

[83] Medium (2023), *Intratec Products Blog*, https://medium.com/intratec-products-blog (23 August 2024).

[84] EMBER Climate (2024), *Türkiye Electricity Review*, https://ember-climate.org/countries-and-regions/countries/turkiye/ (23 August 2024).

[85] Aksay MV, Tabak A. Mapping of biogas potential of animal and agricultural wastes in Turkey. Biomass Convers Biorefin 2022;12:5345–62. https://doi.org/10.1007/s13399-022-02538-6.

[86] Olateju B, Kumar A. Techno-economic assessment of hydrogen production from underground coal gasification (UCG) in Western Canada with carbon capture and sequestration (CCS) for upgrading bitumen from oil sands. Appl Energy 2013;111:428–40. https://doi.org/10.1016/j.apenergy.2013.05.014.

[87] Blanco H, Nijs W, Ruf J, Faaij A. Potential for hydrogen and Power-to-Liquid in a low-carbon EU energy system using cost optimization. Appl Energy 2018;232:617–39. https://doi.org/10.1016/j.apenergy.2018.09.216.

[88] Rashidi NA, Yusup S. An overview of activated carbons utilization for the post-combustion carbon dioxide capture. J CO2 Util 2016;13:1–16. https://doi.org/10.1016/j.jcou.2015.11.002.

[89] Halloran JW. Extraction of hydrogen from fossil fuels with production of solid carbon materials. Int J Hydrogen Energy 2008;33:2218–24. https://doi.org/10.1016/j.ijhydene.2008.02.074.

[90] Koj JC, Schreiber A, Zapp P, Marcuello P. Life Cycle Assessment of Improved High Pressure Alkaline Electrolysis. Energy Procedia 2015;75:2871–7. https://doi.org/10.1016/j.egypro.2015.07.576.

[91] Carapellucci R, Giordano L. Steam, dry and autothermal methane reforming for hydrogen production: A thermodynamic equilibrium analysis. J Power Sources 2020;469:228391. https://doi.org/10.1016/j.jpowsour.2020.228391.

[92] Man Y, Yang S, Xiang D, Li X, Qian Y. Environmental impact and techno-economic analysis of the coal gasification process with/without CO_2 capture. J Cleaner Prod 2014;71:59–66. https://doi.org/10.1016/j.jclepro.2013.12.086.

[93] Tlili O, Mansilla C, Frimat D, Perez Y. Hydrogen market penetration feasibility assessment: Mobility and natural gas markets in the US, Europe, China and Japan. Int J Hydrogen Energy 2019;44:16048–68. https://doi.org/10.1016/j.ijhydene.2019.04.226.

[94] U.S. Department of Energy (2021), *Energy Earth Shot - Hydrogen Shot*, https://www.energy.gov/eere/fuelcells/hydrogen-shot (23 August 2024).

[95] EMBER Climate (2024), *Saudi Arabia Electricity Review*, https://ember-climate.org/countries-and-regions/countries/saudi-arabia/ (23 August 2024).

[96] BASF (2021), *Methane Pyrolysis – a potential new process for hydrogen production without CO_2 emission*, https://arpa-e.energy.gov/sites/default/files/2021-01/16%20OK%20-%20ARPA-E%20Meeting%20Bode%20Flick%20Methane%20Pyrolysis%20web.pdf (23 August 2024).

[97] He G, Bluemling B, Mol APJ, Zhang L, Lu Y. Comparing centralized and decentralized bio-energy systems in rural China. Energy Policy 2013;63:34–43. https://doi.org/10.1016/j.enpol.2013.06.019.

[98] Xie K, Li W, Zhao W. Coal chemical industry and its sustainable development in China. Energy 2010;35:4349–55. https://doi.org/10.1016/j.energy.2009.05.029.

[99] Baris K, Kucukali S. Availibility of renewable energy sources in Turkey: Current situation, potential, government policies and the EU perspective. Energy Policy 2012;42:377–91. https://doi.org/10.1016/j.enpol.2011.12.002.

[100] Filippov SP, Keiko AV. Coal Gasification: At the Crossroads. Economic Outlook Therm Eng 2021;68:347–60. https://doi.org/10.1134/S0040601521050049.

[101] Wilhelm DJ, Simbeck DR, Karp AD, Dickenson RL. Syngas production for gas-to-liquids applications: technologies, issues and outlook. Fuel Process Technol 2001;71:139–48. https://doi.org/10.1016/S0378-3820(01)00140-0.