

# Hydrogen and hydrogen-derived fuels through methane decomposition of natural gas – GHG emissions and costs

Sebastian Timmerberg<sup>a,b,\*</sup>, Martin Kaltschmitt<sup>a</sup>, Matthias Finkbeiner<sup>b</sup>

<sup>a</sup> Hamburg University of Technology, Germany

<sup>b</sup> Technische Universität Berlin, Germany

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## ABSTRACT

Hydrogen can be produced from the decomposition of methane (also called pyrolysis). Many studies assume that this process emits few greenhouse gas (GHG) because the reaction from methane to hydrogen yields only solid carbon and no CO<sub>2</sub>. This paper assesses the life-cycle GHG emissions and the levelized costs for hydrogen provision from methane decomposition in three configurations (plasma, molten metal, and thermal gas). The results of these configurations are then compared to electrolysis and steam methane reforming (SMR) with and without CO<sub>2</sub> capture and storage (CCS). Under the global natural gas supply chain conditions, hydrogen from methane decomposition still causes significant GHG emissions between 43 and 97 g CO<sub>2</sub>-eq./MJ. The bandwidth is predominately determined by the energy source providing the process heat, i.e. the lowest emissions are caused by the plasma system using renewable electricity. This configuration shows lower GHG emissions compared to the “classical” SMR (99 g CO<sub>2</sub>-eq./MJ) but similar emissions to the SMR with CCS (46 g CO<sub>2</sub>-eq./MJ). However, only electrolysis powered with renewable electricity leads to very low GHG emissions (3 g CO<sub>2</sub>-eq./MJ). Overall, the natural gas supply is a decisive factor in determining GHG emissions. A natural gas supply with below-global average GHG emissions can lead to lower GHG emissions of all methane decomposition configurations compared to SMR. Methane decomposition systems (1.6 to 2.2 €/kg H<sub>2</sub>) produce hydrogen at costs substantially higher compared to SMR (1.0 to 1.2 €/kg) but lower than electrolyser (2.5 to 3.0 €/kg). SMR with CCS has the lowest CO<sub>2</sub> abatement costs (24 €/t CO<sub>2</sub>-eq., other > 141 €/t CO<sub>2</sub>-eq.). Finally, fuels derived from different hydrogen supply options are assessed. Substantially lower GHG emissions, compared to the fossil reference (natural gas and diesel/gasoline), are only possible if hydrogen from electrolysis powered by renewable energy is used (> 90% less). The other hydrogen pathways cause only slightly lower or even higher GHG emissions.

## 1. Introduction

In the light of climate change mitigation and the resulting urge to decrease greenhouse gas (GHG) emissions, hydrogen is seen as an important component for future energy systems because its energetic use does not lead to direct CO<sub>2</sub> emissions. Additionally, hydrogen as an energy carrier shows a broad range of existing and potential use cases, e.g., within the electricity, transport, industrial, and heating sector. It can be directly used as hydrogen or alternatively used to synthesize hydrocarbons used as fuels similar to natural gas or diesel/gasoline, within existing supply chains and applications [1–6].

A pre-requisite for an increased hydrogen use, in the context of climate change mitigation efforts, is hydrogen provision with zero or at least low GHG emissions. The most prominent technological concepts

are the hydrogen production from natural gas through steam methane reforming (SMR) combined with CO<sub>2</sub> capture and storage (CCS) and water electrolysis powered by electricity from renewable sources of energy [7–10]. Thus far, both processes play only a minor role within global hydrogen production. Only 12 large-scale CCS projects are in progress globally [11] of which 2 are related to hydrogen [12]. Furthermore, hydrogen from water electrolysis covers less than 1% of the global hydrogen demand [1].

Another option for hydrogen production with potentially low GHG emissions is the decomposition of methane from natural gas sometimes referred to as pyrolysis. This process decomposes methane into its elements hydrogen and solid carbon ( $\text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2$ ). The carbon is not combusted within this process; i.e. the GHG CO<sub>2</sub> is not produced. Instead, the provided solid carbon can be disposed under demarcation

\* Corresponding author at: Eissendorfer Str.40, 21073 Hamburg, Germany.

E-mail address: [sebastian.timmerberg@tuhh.de](mailto:sebastian.timmerberg@tuhh.de) (S. Timmerberg).

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from the biosphere (i.e. GHG neutral). Alternatively, the carbon could be used as a raw material (e.g. as carbon black [13,14]) contributing to the short or long term atmospheric CO<sub>2</sub> inventory.

Different configurations of methane decomposition processes have been studied and a limited number of these processes have been brought to the market. These conversion processes show substantial differences in the selection of energy supply, reactor layout, and used catalyst [15,16].

The available assessments of such methane decomposition systems do not draw a clear picture about hydrogen GHG emissions and costs due to (e.g.) a wide range of technological parameters and different assumptions on the energy supply chain. Parkinson et al. (2019) [7] published a study considering steam methane reforming (SMR), coal and biomass gasification, electrolysis, and nuclear hydrogen supply technologies. Only limited attention is given to methane decomposition processes by considering only a generic configuration with an overall process efficiency of 53% related to the higher heating value (HHV). The configuration combusts natural gas for the required process heat. Under the assumption of a natural gas supply chain characterized by lower than average global GHG emissions, methane decomposition is found to produce hydrogen with GHG emissions of 6.1 kg CO<sub>2</sub>-eq./kg H<sub>2</sub> being 52% lower than hydrogen from steam methane reforming (SMR). Methane decomposition is identified as the hydrogen technology with lowest CO<sub>2</sub> abatement cost among all investigated alternatives.

These results are based on a preceding study investigating hydrogen production costs and GHG emissions of a methane decomposition system using a molten metal reactor with a catalytic active Ni-Bi alloy [17]. Also here, methane decomposition produces hydrogen at low costs and lower costs than the alternative steam methane reforming (SMR) with CO<sub>2</sub> capture and storage (CCS). At a low CO<sub>2</sub> emission price above ca. \$30/t CO<sub>2</sub>, methane decomposition is found to produce hydrogen at an economically competitive level to steam methane reforming.

Parkinson et al. (2017) [18] investigate a molten metal reactor that applies molten iron. The process heat is provided either by combustion of natural gas, hydrogen, or the application of an electric arc [18]. As no natural gas supply chain GHG emissions are considered here, hydrogen production is characterized by very low GHG emissions (0 to 3.1 kg CO<sub>2</sub>-eq./kg H<sub>2</sub>). However, the configuration of the methane decomposition system (i.e. choice of the energy source providing the process heat) has shown to have a strong impact on the GHG emissions. The system using hydrogen is found to emit the lowest GHG emissions and the process applying an electric arc has highest. Hydrogen production costs by methane decomposition are in the same range or even lower than from steam methane reforming. One reason is that solid carbon (mostly carbon black) is considered to be a valuable and marketable product. However, the carbon black and a potential use (i.e. the eventual release of the CO<sub>2</sub> into the atmosphere by increasing GHG emissions) is not considered further.

Another configuration of a methane decomposition process is the use of plasma reactors. One example is the Kvaerner CB&H process. Existing literature focuses primarily on hydrogen production costs, and life-cycle GHG emissions are not considered. However, a low climate impact of this process is assumed due to the reaction chemistry leading to no direct CO<sub>2</sub> emissions [16,19–23]. Low hydrogen production costs result from methane decomposition. This is especially true if a revenue for the produced carbon is considered. Different approaches are used to determine the hydrogen costs in relation to the carbon black selling price. Dagle et al. (2017) [16] compare the hydrogen production costs to the DOE cost targets of \$4/kg. A small-scale plasma methane decomposition system is found to produce hydrogen only below the cost target if the carbon product is sold at more than ca. \$0.9/kg carbon. The hydrogen costs of \$6 to \$7/kg result if the produced carbon is not sold [14,19]. Furthermore, the impact of the production capacity is investigated and hydrogen costs between \$6/kg for large-scale up to \$14/

kg for small-scale systems are concluded (no revenue from the carbon product) [22]. The carbon is partly seen as the main product and hydrogen only as a by-product that is (e.g.) combusted in a gas-fired power plant [19].

Methane decomposition systems can also use gas reactors either with or without catalysts. Zhang et al. (2018) [24] use a least cost linear optimisation model to identify optimal reactor design parameters. The model is applied in four scenarios defined by different assumptions about a potential catalyst regeneration (e.g. non-oxidative regeneration of catalyst is available) as well as the value of the carbon product (disposal vs. selling). The provided hydrogen is subsequently used in a fuel cell for electricity generation. If the catalyst cannot be regenerated, electricity costs and GHG emissions are higher than the electricity production in combined cycle power plants combusting natural gas and applying CO<sub>2</sub> capture and storage (CCS). If catalyst regeneration is available, methane decomposition and a combined cycle power plant with CO<sub>2</sub> capture and storage (CCS) emit similar amounts of GHG. However, methane decomposition leads to much higher CO<sub>2</sub> abatement costs, e.g., due to the fuel cell. Furthermore, a heat exchange gas reactor is assessed for methane decomposition [9,10,13,25]. Such a reactor uses the flow of a solid bed material in the opposite direction of the gas enabling a heat exchange between gas leaving and entering the reactor. This concept is compared with two thermal gas reactors, one using a catalyst and the other one not. The hydrogen is used in a gas turbine for electricity generation. The reference is an electricity provision from a natural gas-fired power plant. Even the best methane decomposition configuration requires a carbon revenue of 600 to 700 €/t to reach cost parity [9]. A different study examines various heat exchange gas reactor systems with electrolysis as well as steam methane reforming partly including CO<sub>2</sub> capture and storage. In a small-scale hydrogen production scenario, methane decomposition is found to produce hydrogen at similar costs to electrolysis and even significantly lower costs than small-scale steam methane reforming (SMR). If the produced carbon is used for steam gasification, hydrogen costs are 54% lower compared to steam methane reforming and 24% lower than electrolysis [10].

The combination of methane decomposition within a gas reactor with hydrogen processing to gasoline via methanol synthesis is evaluated by Machhammer et al. (2018) [26]. Hydrogen is alternatively delivered from electrolysis powered by electricity from wind turbines or fossil-based electricity from the grid. Hydrogen delivery from methane decomposition is found to produce gasoline at 35 to 50% lower costs than wind powered electrolysis, but with similar GHG emissions.

While many studies conclude positive economic effects of methane decomposition against alternative hydrogen production pathways, no publication exists covering the bandwidth of different methane decomposition systems. Thus, no publication investigates the impact of system configurations on GHG emissions as well as on costs. Only one review study [15] is available comparing the technological status of different methane decomposition configurations. However, no comparative study brings together the technological and economic assumptions made in different studies. Therefore, there is not a study comparing the different methane decomposition systems regarding costs and GHG emissions under similar boundary conditions. This study aims at filling this research gap. Accordingly, this assessment encompasses the following research questions:

- What are central differences between various methane decomposition process configurations currently under discussion?
- Which impact do these differences have regarding GHG emissions and hydrogen production costs?

Existing studies about single methane decomposition configurations conclude a bandwidth of GHG emissions and costs. Higher and lower hydrogen costs as well as GHG emissions with competing technologies are found. The performance of the different methane decomposition system configurations is thus also compared to alternative hydrogen

production technologies. The following additional questions arise:

- How does hydrogen provision from methane decomposition perform regarding GHG emissions and costs compared to steam methane reforming (SMR), SMR with carbon dioxide capture and storage (CCS), and water electrolysis?
- What are the CO<sub>2</sub> abatement costs for hydrogen production and derived fuels?

As the hydrogen production and use is discussed through a climate change mitigation perspective, the performance of methane decomposition systems is discussed in the context of a large-scale implementation within the global energy system. The impact of this general boundary condition is discussed in detail.

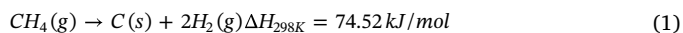
The analysis is structured as follows: first, a literature review on considered technologies including techno-economic parameters is presented in section 2 and contains a description of three methane decomposition technology configurations (i.e. plasma, molten metal, and thermal gas reactor systems). Then in section 3, alternative hydrogen production technologies (SMR and CCS, electrolysis) competing with these methane decomposition technologies are presented. Both sections include a discussion of selected techno-economic parameters. To provide comparable data the chemical engineering plant cost index (CEPCI) is used to adjust economic parameters to €<sub>2018</sub> values. Deviations in the literature values are discussed and a consistent parameter set is derived for each technology. Subsequently, section 4 presents the overall methodology and system boundaries used to assess hydrogen cost, GHG emissions, and CO<sub>2</sub> abatement costs. Then the different supply chains considered are defined within section 5. The results are discussed in section 6. Section 7 includes a sensitivity analysis as assumptions that show spatial differences can have a strong impact on the results. This contains an additional analysis of the consequences of the produced solid carbon being considered as a product (i.e. carbon black). Section 8 shows costs, GHG emissions, and CO<sub>2</sub> abatement costs if the hydrogen produced by the different technologies assessed so far is used for the production of the hydrocarbon-based fuels methane and gasoline/diesel (i.e. substitutes for fuels based on crude oil and/or natural gas). Finally, the most important findings are summarized and discussed.

## 2. Methane decomposition

Methane decomposition (also called methane pyrolysis or methane cracking) is a chemical process splitting methane, or in general hydrocarbons, into its elemental components hydrogen and solid carbon (Equation (1)). The governing reaction is endothermic; the necessary energy can come from different sources of energy.

Methane enters and hydrogen leaves this decomposition process both in a gaseous state, whereas the produced carbon is a solid. Oxygen is not involved at all within this process (i.e. no CO or CO<sub>2</sub> is produced). Thus, for the product gas upgrading there is no need of an additional CO or CO<sub>2</sub> separation. Therefore, this process is less complex than e.g. the “classical” steam methane reforming (SMR) process [27,28]. Depending on the required hydrogen purity and the hydrogen conversion rate, such processes might operate without any additional gas cleaning or upgrading. This might be the case if the produced hydrogen is used purely as a gas for combustion as it is realized within a plant located in Nebraska (Table 2). If a high purity of the provided hydrogen is needed, a subsequent separation step of hydrogen and methane is necessary.

If only hydrogen without the carbon is the desired product, the theoretical efficiency of the process is 59% (Equation (2)). The remaining energy contained originally within the natural gas is stored as carbon. In real applications the efficiency is lower, e.g. due to heat losses. Stoichiometrically, 21 kg of solid carbon are produced per 1 GJ of hydrogen (the higher heating value (HHV) is used as a reference throughout this paper).



$$\eta_{\text{theo}} = \frac{2\text{HHV}(\text{H}_2)}{\text{HHV}(\text{CH}_4) + \Delta H} = 59\% \quad (2)$$

Fig. 2 shows three categories of continuous methane decomposition systems that differ in relation to the reactor type, the use of a catalyst, and the source of process-related energy. Most of the conceivable combinations of reactor type, catalyst, and energy supply can be found in the literature. The technological development status covers all stages between advanced R&D activities to commercially available processes. However, none of these commercially available processes produce carbon and high purity hydrogen simultaneously (Table 2).

### 2.1. Process technologies

Below the process technologies assessed here are described and characterized in detail.

#### 2.1.1. Plasma reactor systems

Plasma is an ionized state of a gas containing free charge carriers (i.e. it is therefore electrically conductive) [29]. Two types of plasma are applied for methane decomposition.

- 1) In a thermal plasma or a “hot” plasma the temperature is homogeneously distributed. The chemical decomposition process of the methane is observed within a high-temperature environment allowing it to reach chemical equilibrium.
- 2) In a non-thermal or “cold” plasma, the electrons show a much higher temperature than the heavier species such as neutrons and electrons (i.e. the electrons can have temperatures of several 10,000°K whereas the complete gas is much colder (e.g. room temperature) [29,30].

Based on these two plasma types, plasma applications for methane decomposition are classified into cold (less than 1,000 K) and hot (> 1,000 K) processes. Cold plasma processes typically show lower conversion efficiencies compared to hot plasma processes [16]. However, cold plasma processes show a higher selectivity compared to hot plasma processes [31]. Possible by-products of the methane decomposition reaction include ethyne, benzene, and ethane [13,32]. Most plasma systems operate without a catalyst [16].

Distinct advantages of plasma processes are the low inertia and the fast start up of the system; i.e. plasma processes could most likely be combined with a fluctuating electricity supply from renewable energy sources of such as wind power or solar radiation. Furthermore, only limited methane purification is needed [30,31].

Several plasma processes for methane decomposition have been developed in recent years (Table 2). The most prominent examples are the Kvaerner process and the process of Monolith Materials both using a hot plasma generated through graphite coils targeting carbon black production. In both processes, the hydrogen is only by-product (Table 2).

#### 2.1.2. Molten metal reactor systems

Also in molten metal reactors methane is split into hydrogen and carbon black. Here, methane is injected at the bottom of a reactor containing liquid metal at high temperatures and hydrogen leaves the reactor at the top.

This concept shows two significant benefits:

- 1) The molten metals allow an efficient heat transfer.
- 2) Carbon black rises to the surface of the metal allowing for simple carbon removal [15].

Different reactor materials such as stainless steel and quartz glass

**Table 1**  
Techno-economic parameters of considered thermal decomposition configurations derived from literature (values in brackets indicate bandwidth).

Reactor concept	Catalyst	Heat supply	Carbon yield [kg C/kg H <sub>2</sub> ]	Electricity consumption [kWh/kg H <sub>2</sub> ]	CH <sub>4</sub> consumption [MJ/kg H <sub>2</sub> ]	Investment [€/(kg/h H <sub>2</sub> )]	Annual O&M cost [% of Invest.]
Thermal plasma	No	Thermal plasma	3.0	13.9 (11.1 – 17.8)	223.0 (222.1 – 242.3)	27,750 (3,331–151,914)	3.0
Molten metal	Yes	CH <sub>4</sub>	3.0	0.0 (0.5 – 0.3)	272.7 (252.6–272.7)	26,934 (23,233–30,634)	
Gas reactor	No	CH <sub>4</sub>	3.0	0.0 (0–2.3)	299.0 (266.8–332.5)	19,822 (8,506–36,073)	

have been tested with different molten metals such as tin, lead, and copper [33,34]. Also, the use of iron has been investigated theoretically [18]. Experiments show that higher temperatures lead to higher hydrogen yields [34]. By using a catalytic active metal alloy (Ni, Bi), the yield of hydrogen can be increased [35]. The produced carbon ascending to the surface of the molten metal may contain traces of the metal potentially requiring additional cleaning steps [35]. Heating of the metal and/or the heat transfer medium can be achieved through burning of natural gas or hydrogen, by electricity based resistant heating, by inductive heating, or through an electric arc.

The company Arenius developed a pilot-scale system applying molten metal reactors for methane decomposition [16] (Table 2). Further information is not available on other activities of molten metal applications for methane decomposition.

### 2.1.3. Conventional gas reactor systems

Methane decomposition is also investigated in conventional gas reactors such as tubular fixed-bed and fluidized-bed reactors. Additionally, processes with and without metal and carbon-based catalysts have been assessed. But both types of catalysts show fast deactivations as the produced carbon black is deposited on the catalysts' active parts [36].

Separating the carbon deposited on the catalyst surface and re-activating the catalyst is challenging. Combusting the carbon off the catalyst is one possibility [15,37]. Alternatively, the carbon can be used for additional hydrogen production through gasification with water vapour (i.e. Boudouard reaction and water–gas-shift-reaction) [10,28]. However, both concepts result in solid carbon being converted to CO<sub>2</sub> and therefore contradicting the idea of reducing the CO<sub>2</sub> emissions.

The use of a carbon-based catalyst is still in an early R&D stage. Pilots have been utilizing metal-based catalyst or not using any catalyst at all [15]. Universal oil products developed the Hypro process using a fluidized-bed reactor with a Ni catalyst at 1,150 K followed by a catalyst regeneration with air; i.e. only hydrogen and not carbon was produced [37] (Table 2).

### 2.2. Techno-economic parameters

Table 3 compiles information on configurations, energy balance, and the cost of different methane decomposition systems segmented into plasma, molten metal, and gas reactor systems.

- Plasma systems. Most of the identified studies assess plasma systems. Investment estimations cover a broad range, which cannot be explained by the difference in considered cost elements because only one source provides this information (Fig. 3). The required electricity as well as methane demand is, in most cases, estimated close to the theoretical minimum of 221 MJ<sub>Methane</sub>/kg H<sub>2</sub>.
- Molten metal systems. Economic parameters available for such systems do not show a very broad range because the available parameters come from a similar research group. Also, the bandwidth of investments for configurations with conventional reactors is rather narrow. The given difference is most likely due to the assumption of different reactor systems; i.e. low costs result from a rather simple gas reactor compared to high cost caused by a complex heat exchange reactor. The required energy demand depends also on the choice of the energy source. Again, methane demand is close to the theoretical minimum if electric heating is applied.
- Gas reactor systems. The costs of the catalyst used within these systems are only taken into account as initial costs [9,10,24,26]; i.e. no regular renewal of the catalyst is considered. Only one study considers that a regeneration of the catalyst might not be available, and thus the catalyst needs to be renewed [24]. If no regeneration is available, a carbon catalyst leads to lower cost than the application of a Ni-based catalyst. Still, the carbon catalyst costs alone are 4.0 €/kg H<sub>2</sub> (assuming catalyst costs of 0.95 €/kg and an expected catalyst demand of 0.7 kg carbon/kg catalyst [24]).



**Table 2**  
Commercial methane decomposition projects.

Process; company name	Project development status	Process / project information
CarbonSaver; Atlantic hydrogen [38,39]	Pilot plant commissioned in 2009 in New Brunswick (Canada); demonstration plant announced	- Production of hydrogen enriched natural gas (ca. 20% hydrogen) and carbon black - Thermal plasma torch reactor operating at 1750 – 2800 K
BASF, Liden and Thyssen-Krupp [26]		- Non-catalytic methane decomposition - High degree of heat integration
CB&H; Kvaerner [16,19,20,31]	Pilot plant commissioned in 1992 (2000 Nm <sup>3</sup> /h H <sub>2</sub> ); Demonstration plant (7600 Nm <sup>3</sup> /h H <sub>2</sub> ) built in Canada but decommissioned without operation	- Production of carbon black and hydrogen - Flexible feedstock; natural gas to heavy oil residues
GasPlas [31,40]	No information on further activities of GasPlas available today	- Graphite electrode used - Decentralised hydrogen production for hydrogen refuelling stations
Monolith Materials [41,42]	Pilot plant operating for 4 years until 2018; commercial plant in Nebraska (USA) under construction (announced commissioning in 2020)	- Microwave non-thermal plasma (microwave) operating at atmospheric pressures and 450 – 650 K - Up to 6 kW microwave power was tested
EGT Enterprises [16,43]	Demonstration plant announced	- Production of carbon black; hydrogen is by-product to be used in coal-fired power plant - Thermal plasma process
Carbotopia	Pilot plant operating „several thousand hours“ between 2010 and 2011 (13 kg carbon and 4.3 kg hydrogen per day)	- Production of carbon black and hydrogen - Electrically heated chemical reactor operating at 1350 – 1500 K
HYPRO; Universal Oil Products (UOP) [37]		- Electricity production by hydrogen combustion in gas turbine and by using the carbon in a direct carbon fuel cell - Production of carbon nanotubes and hydrogen - Fluidized bed gas reactor with metal-based catalyst - Production of hydrogen - Fluidized bed reactor with Ni/Al <sub>2</sub> O <sub>3</sub> catalyst operating at 1150 – 1450 K - Regeneration of catalyst through combustion with air

Based on the investigated concepts (Table 3), three concepts with the following basic assumptions are further investigated:

- (1) the plasma reactor applies a thermal plasma powered by electricity,
- (2) the molten metal reactor shows catalytic activity and methane combustion provides heat,
- (3) the gas reactor applies a thermal decomposition (i.e. no catalyst) and methane provides heat.

A set of techno-economic parameters are derived (Table 1) for each of these methane decomposition systems. For all systems, a bandwidth is included covering minimum and maximum values found in the literature. Extreme values are not considered. The available information on the plasma systems falls out of range and a value is derived based on the values for gas reactors as the reactor design shows similarities.

### 3. 3. Reference and alternative hydrogen production

The following presents hydrogen provision systems as a reference and as an alternative for hydrogen production by the methane decomposition discussed in section 2.

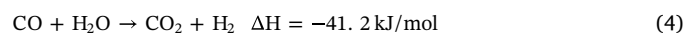
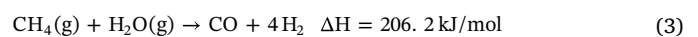
#### 3.1. Steam methane reforming (SMR)

Steam methane reforming (SMR) is the globally dominant hydrogen production process [1]. This process applies four basic steps:

- Contaminants such as sulphur or chloride compounds are removed.
- Methane reacts with water steam yielding carbon monoxide and hydrogen (Equation (3)).
- The hydrogen yield is increased through the reaction between carbon monoxide and additional water steam to carbon dioxide and additional hydrogen (water gas shift reaction, Equation (4))
- The raw hydrogen is purified typically through pressure swing absorption (PSA).

The two chemical reaction steps show a net energy demand (endothermic). It is covered through the combustion of additional methane

plus the tail gas stream leaving the pressure swing absorption (PSA) unit containing mainly CO<sub>2</sub>, H<sub>2</sub>, and some unreacted CH<sub>4</sub> and CO. Steam methane reforming (SMR) processes typically produce excess steam to be used for electricity generation being in the range of the electricity demand (i.e. zero net electricity production results) [8,44–46].



The steam methane reforming (SMR) process can be extended with a CO<sub>2</sub> capture unit to reduce the GHG emissions. This process is characterized by two distinct CO<sub>2</sub> sources: CO<sub>2</sub> production through process chemistry and through energy supply. Thus, removing CO<sub>2</sub> can be achieved at three locations: from the raw hydrogen entering the pressure swing absorption (PSA), from the tail gas leaving the PSA, or from the flue gas leaving the furnace. Depending on the technical configuration between 54 and 90% of the CO<sub>2</sub> can be captured [44,45].

The captured CO<sub>2</sub> needs to be stored in order to avoid its release into the atmosphere. Global storage capacities are estimated between 8,000 and 55,000 Gt CO<sub>2</sub> [47]. For comparison, in 2018 about 37 Gt CO<sub>2</sub> were emitted globally [48]. Based on these optimistic figures even in a 1.5 °C climate change target, global storage capacities will not be a limiting factor in this century [49]. However, spatial distribution of storage possibilities might be a limitation if no sufficient transport chains are established. Pipelines or ships as technically mature options can transport CO<sub>2</sub> to the storage. A subsequent storage of CO<sub>2</sub> is possible in geological formations such as aquifers, in unminable coal seams, or in depleted oil and gas reservoirs. Different concepts have been tested. Still, further experience is needed at scale. One important aspect is a reliable monitoring of injected CO<sub>2</sub>. However, no such CO<sub>2</sub> chain has been established commercially so far, and thus no reliable costs values are available [50].

Techno-economic parameters of large-scale steam methane reforming (SMR) processes are shown in Table 4. Although this process is state of the art, the methane demand shows a considerable range. If CO<sub>2</sub> capture is applied, the average methane consumption increases by 5%. However, also the bandwidth and the uncertainty increases.

**Table 3**  
Techno-economic parameters of different thermal decomposition configurations.

Source	Reactor concept	Catalyst	Heat supply	Nominal H <sub>2</sub> capacity [kg/day]	Carbon yield [kg C/kg H <sub>2</sub> ]	Electricity consumption [kWh/kg H <sub>2</sub> ]	Methane consumption [MJ/kg H <sub>2</sub> ]	H <sub>2</sub> purification or use case	Investment [€/(kg/h H <sub>2</sub> )]	Cost elements in Investment	Annual O&M cost [% of Investment]
<b>Plasma processes</b>											
[19] <sup>a</sup>	TP	No	TP	88,668	3.0	12.2	222.1	n/a	25,336	n/a	1.0%
[16]	TP	No	TP	1,914	3.1	16.1	304.8	n/a	<sup>a</sup> 151,914	n/a	n/a
[22]	TP	No	TP	4,000	3.0	14.3	223.5	PSA	35,470	E, C, I	18.6%
[21]	TP	No	TP	18,263	3.0	17.8	223.5	PSA	<sup>a</sup> 106,354	n/a	3.9%
[20]	TP	No	TP	13,683	2.8	11.7	222.1	n/a	<sup>a</sup> 111,568	n/a	5.0%
[23]	TP	No	TP	402,901	3.0	<sup>a</sup> 11.1	242.3	n/a	3,331	n/a	2.0%
<b>Molten metal systems</b>											
[18]	MM	No	EA	547,945	3.0	14.3	222.1	PSA	26,487	E, F	5.0%
	MM	Future	EA	547,945	3.0	<sup>a</sup> 6.5	222.1		23,974		
	MM	catalytic	CH <sub>4</sub>	547,945	3.0	0.0	252.6		23,233		
	MM	molten metal	H <sub>2</sub>	547,945	3.7	0.0	274.3		24,386		
[17]	MM	Ni-Bi	CH <sub>4</sub>	273,973	3.0	−0.5	272.7	PSA	30,634	E, I, M	2.0%
<b>Gas reactor systems</b>											
[26]	BR	No	EH	27,397	3.0	7.2	222.1	n/a	<sup>a</sup> 32,850	n/a	n/a
[24] <sup>b</sup>	FBR	Nickel	CH <sub>4</sub>	253,950	3.0	2.3	332.5	PSA	13,798	E, I, P, C	4.0%
	FBR	Carbon					294.7		13,892		
	FBR	No					294.7		13,892		
[9]	GR	No	CH <sub>4</sub>	26,344	3.0	0.0	306.3	Product gas for	11,268	E, I, P	2.0%
	GR	No	EH	22,698	3.0	17.7	224.4	electricity	8,506		2.0%
	FBR	Nickel	Carbon	26,002	1.7	1.2	221.4	production	25,604		2.0%
	HER	No	EH	19,358	3.0	19.8	228.8		12,463		2.0%
[10]	HER	No	CH <sub>4</sub>	2,158	3.5	0.0	266.8	Membrane	35,962	E,C	2.0%
	HER + G	No	CH <sub>4</sub>	2,158	0.5	0.3	155.6		26,263		2.0%

All values given in higher heating values; Abbreviations: TP: Thermal plasma, MM: Molten metal, BR: Batch reactor, FBR: Fluidized bed reactor, GR: Gas reactor, HER: Heat exchange reactor, G: Gasification, EA: Electric arc, EH: electric resistance heating, E: Equipment, F: Factor used to come from equipment cost to investment, no detailed information on cost elements, C: Contingency, I: Civil cost, P: Project cost such as engineering or management

a: Mean value presented, bandwidth is presented in source

b: Methane demand in study is less than theoretical limit; adjusted to minimal methane demand based on reaction equation

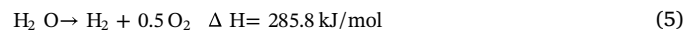
c: Hydrogen is used in fuel cell for electricity production, associated cost are subtracted; Case with Ni assumes that technology exists to separate carbon from Ni

Additionally, due to the CO<sub>2</sub> capture, the overall electricity consumption of the process increases but it remains of minor importance compared to the demand for methane. The average investment increases by 16%, however the bandwidth and the uncertainty increases.

Table 5 shows techno-economic parameters of steam methane reforming (SMR) with and without carbon capture. The costs of the necessary CO<sub>2</sub> transport and storage are estimated to 10 €/t CO<sub>2</sub> [45,46,51].

### 3.2. Electrolysis

Water electrolysis is an electrochemical process splitting water into hydrogen and oxygen. Direct current powers this endothermal reaction (Equation (5)). The process does not lead to direct CO<sub>2</sub> emissions. Thus, this option represents an alternative hydrogen production pathway with potentially low GHG emissions.



**Table 4**  
Techno-economic parameters of steam methane reforming (SMR) without and with carbon capture technology (CCS).

	Nominal H <sub>2</sub> capacity [kg/day]	CCS technology	Rate of CO <sub>2</sub> captured from total	Electricity consumption [kWh/kg H <sub>2</sub> ]	Methane consumption [MJ/kg H <sub>2</sub> ]	Investment [€/(kg/h H <sub>2</sub> )]
<b>SMR (without carbon capture)</b>						
[52]	1,102,032	no	0%	0.2	175.1	8,537
[53]	379,387	no	0%	0.6	215.9	12,583
[54]	503,686	no	0%	0.0	211.0	11,518
[8] <sup>b</sup>	324,202	no	0%	0.4	192.4	9,415
[4]	162,101	no	0%	0.0	203.1	19,213
[7]	n/a	no	0%	0.0	189.0	14,780
[45]	215,856	no	0%	−1.1	175.5	19,007
<b>SMR with carbon capture</b>						
[52]	1,200,000	amine	90%	1.3	185.3	11,164
[53]	379,387	amine	90%	1.1	215.9	14,575
[54]	503,686	amine	<sup>a</sup> 90%	0.0	288.7	39,715
[8] <sup>c</sup>	324,202	amine	56%	1.0	177.6	10,712
[45]	215,856	amine	90%	0.0	192.8	33,948

<sup>a</sup> related to flue gas

<sup>b</sup> process produces 37 MJ/kg H<sub>2</sub> of steam

<sup>c</sup> process provides 11 MJ/kg H<sub>2</sub> of steam

**Table 5**

Techno-economic parameters of considered steam methane reforming (SMR) with and without carbon capture derived from literature review (values in brackets indicate bandwidth).

	CO <sub>2</sub> captured from total	Electricity consumption [kWh/kg H <sub>2</sub> ]	Methane demand [MJ/kg H <sub>2</sub> ]	Investment [€/kg/h H <sub>2</sub> ]
<b>SMR (without carbon capture)</b>	0%	0 (-1.1 – 0.6)	185.6 (175.1 – 215.9)	12,583 (8,537–19,213)
SMR with carbon capture	90%	0.9 (0 – 1.3)	194.9 (177.6–288.8)	14,573 (10,712 – 39,715)

So far, two main electrolysis technologies are applied on a utility-scale: the alkaline and the proton exchange membrane electrolysis. Solid oxide electrolyzers are demonstrated so far on a small-scale only.

- Alkaline electrolysis uses a water based alkaline solution (KOH or NaOH) as an electrolyte. Alkaline systems can be operated under transient conditions and down to partial loads between 20 and 40% [55]. After roughly 90,000 h (7 to 12 a) of operation, the electrodes and diaphragms need to be replaced [55,56].
- Proton exchange membrane (PEM) electrolysis uses a membrane as an electrolyte. System efficiencies are between 47 and 86%; this is the same order of magnitude compared to the alkaline electrolysis technology. However, such electrolyzers show a better performance when operated based on electricity with a fluctuating behaviour.

Since the investment costs of proton exchange membrane (PEM) electrolyser systems are substantially higher compared to alkaline systems, in the next sections only the latter are considered [55–57]. For the respective hydrogen provision systems, the overall efficiency from electricity to hydrogen covers a range between 74 and 77%. The costs also cover a broad bandwidth (Table 6). For the following calculations a stack replacement after 10 years is assumed [57] costing 50% of the initial investment [58].

#### 4. Methodology

The target of this paper is to compare different technologies for hydrogen production with a focus on methane decomposition systems. Additionally, the hydrogen production pathways are compared to the case that the hydrogen is further processed to liquid hydrocarbon fuels (e.g. gasoline, Diesel) and to the gaseous fuel methane (i.e. crude oil and natural gas substitutes). Hydrogen and fuel production are evaluated regarding cost and GHG emissions throughout the lifetime of the production plants. The following utilizes the current dominating production pathways for comparison purposes.

A framework for a comprehensive comparison is set-up considering a near-term and large-scale implementation of these processes (i.e. for a hydrogen and fuel production in quantities relevant to the global energy industry and thus the climate) (Fig. 1). Energy supply chains are selected accordingly and cover current global average conditions. The electricity supply is considered in two cases that can be implemented worldwide. Either the hydrogen production receives electricity from the existing power grid or a separate electricity supply based on renewable sources of energy. The energy supply reflects the status of the energy systems regarding cost and emission related factors. Techno-economic parameters for hydrogen production technologies and auxiliaries are

derived from the literature reflecting large-scale, state-of-the art technology (section 2 and 3). Besides an average value, a bandwidth of techno-economic parameters of hydrogen production technologies are assumed in order to account for technology related uncertainties. The calculations are also conducted for the minimum and maximum values of the bandwidth and displayed as error bars in the results.

Hydrogen production through methane decomposition produces solid carbon as a by-product. It can potentially be sold as carbon black. However, a large-scale hydrogen production, as considered here, significantly exceeds the carbon black market size. Thus, no further use of the solid carbon is considered; i.e. this carbon is disposed to avoid an impact on global climate. Nevertheless, the impact of marketing carbon black for hydrogen production in much smaller quantities is addressed in an excursus. The boundary conditions can show significant regional differences (e.g. financial parameters, natural gas supply chain emissions). Resulting deviations in cost and GHG emissions are discussed within a sensitivity analysis.

The levelized cost of hydrogen *LCOH* and of the subsequent provided fuel *LCOF* are used as estimates for hydrogen and fuel costs (Equation (6)). They consider the costs of the production plant  $c_p$ , the costs of energy powering the hydrogen and subsequent fuel production, and the costs for operation and maintenance  $c_{o\&m}$ . Costs are considered on an annual basis and normalized by the annual production of hydrogen  $p_h$  respectively of fuel  $p_f$ . The weighted average cost of capital *WACC* is used to annualize the cost of the production plant.

GHG emissions are estimated based on the carbon footprint approach [60] using global warming potentials (GWP) with a 100 year time horizon [61]. Natural gas/methane is a major input for some of the considered hydrogen production processes. Methane is a short-lived gas and therefore shows a stronger radiative forcing over a shorter time-period. Thus, the impact of a shorter time-period (20 years) on the GHG emission estimation is considered in the sensitivity analysis (section 7).

CO<sub>2</sub> abatement cost are derived from the levelized costs and the GHG emission estimations by setting GHG emission reductions in relation to additional cost (Equation (7)). The reference *ref* are currently dominant production pathways (i.e. hydrogen produced through steam methane reforming and fossil fuels). Table 7 summarizes variables and indices.

$$LCOH \text{ or } LCOF = \frac{\frac{c_p}{\sum_{n=1}^N \frac{1}{(1+WACC)^n}} + c_e + c_{o\&m}}{p_{h \text{ or } f}} \quad (6)$$

$$CO_2 \text{ abatement cost}_i = \frac{LCOH/F_i - LCOH/F_{ref}}{GHG_{ref} - GHG_i} \quad (7)$$

**Table 6**

Techno-economic parameters of alkaline electrolysis systems (values in brackets show published bandwidth).

	Electricity consumption [kWh/kg H <sub>2</sub> ]	Investment [€/kg/h H <sub>2</sub> ]
[6]	51.3 (48.3–77.5)	61,063 (31,376 – 218,174)
[59]	52.6	60,765
[7]	51.4	41,217 (20,518 – 51,294)
[58]	53.6 (48.0 – 60.6)	28,127 (21,610 – 36,349)
Own assumptions	52.2 (48.0–77.5%)	47,928 (19,370 – 218,174)

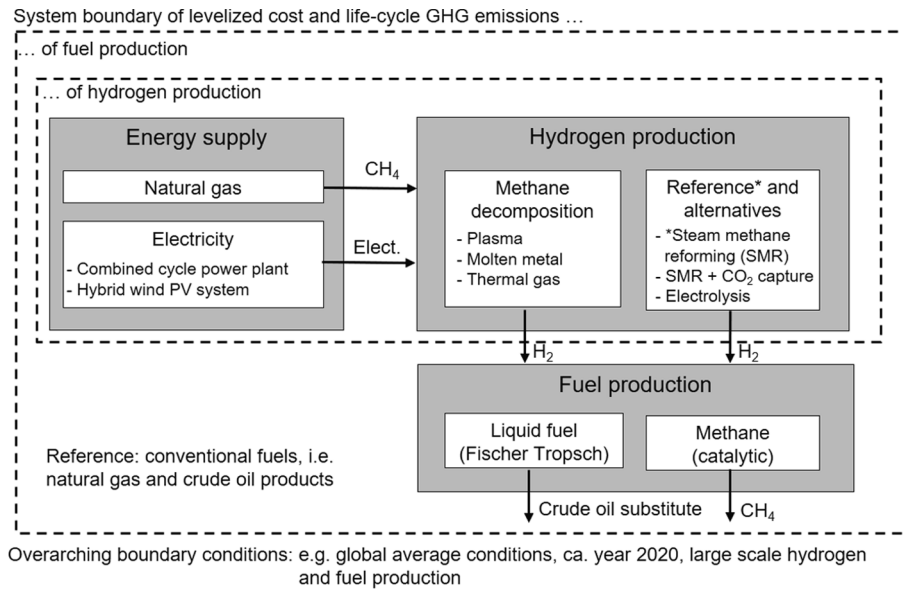


Fig. 1. (Graphical abstract) System boundaries and setup as well as major assumption.

## 5. Data

The technology and energy supply chain input data that is used for the subsequent assessments are presented below, following the definitions in the methodology (section 4) about the hydrogen production and subsequent fuel production. Table 8 gives an overview about considered cases and input data.

Throughout the calculations, a weighted average cost of capital (WACC) of 5% is assumed. The economic lifetime is defined to be 30 years for power and chemical plants; it is 20 years for PV systems and wind turbines.

### 5.1. Electricity supply

Electricity is provided by two variants:

- (1) Gas combined cycle (CC) power plants with a high capacity utilization reflecting global power generation systems based on fossil energy;
- (2) Renewable sources of energy globally available (i.e. wind and solar irradiation) without any connection to the grid.

Electricity production in gas combined cycle power plants provides electricity with a high overall efficiency of 59%. Investments are assumed to be 815 €/kW and annual non-energy related O&M costs sum up to 19 €/kW a [62]. Furthermore, a capacity factor (i.e. share of actual energy output compared to theoretical maximum output per year) of 95% is defined.

Electricity production from renewable sources of energy is achieved with a combined wind and photovoltaic (PV) system. Average investment are 1,025 €/kW for PV and 1,269 €/kW for wind turbines in 2018 [63]. O&M cost are estimated to be 1.5% for wind turbines and 0.5% for PV systems related to the overall investment costs [2]. A capacity factor of 40% for wind and 20% for PV electricity production are assumed to being slightly above global average [63] as state of the art technology is assumed. A combination of wind and PV technology yields a higher capacity factor of 57% compared to the respective individual systems as these energy sources show a small temporal overlap estimated to sum up to 5% [64].

GHG are emitted during manufacturing, assembly, and operation of these electricity provision systems. For onshore wind turbines, a value of 6 g CO<sub>2</sub>-eq./kWh is assumed for electricity production [65]. GHG emissions of electricity production from PV technologies are assumed to

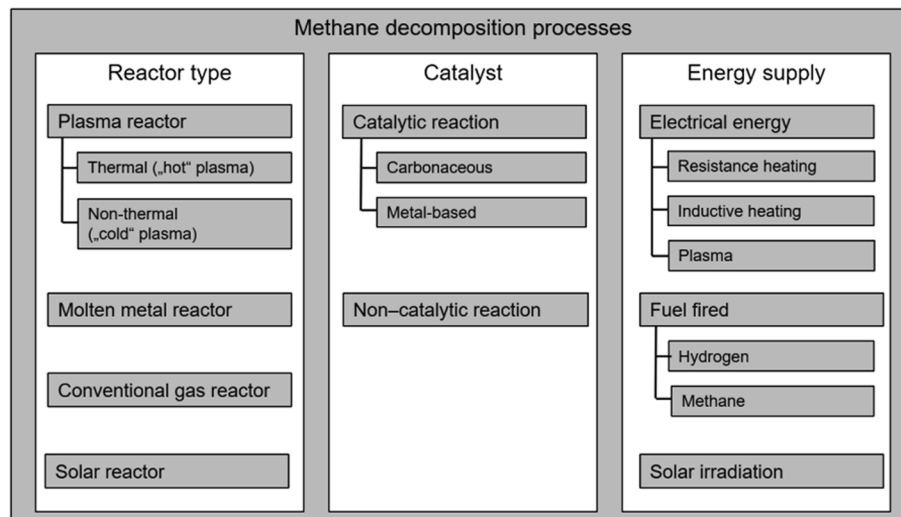
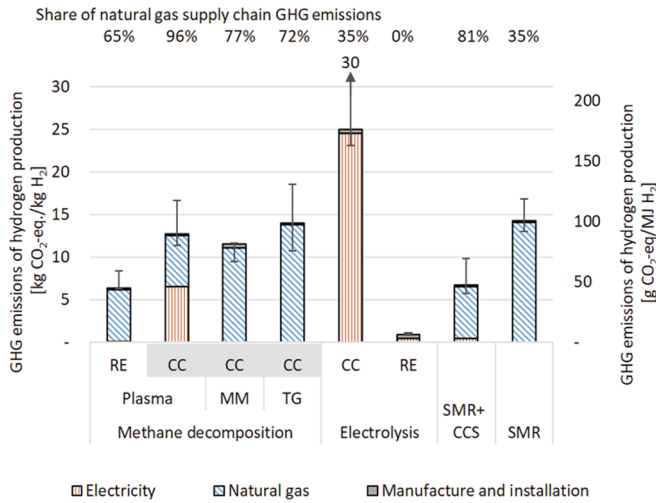


Fig. 2. Categories of methane decomposition processes.





**Fig. 3.** GHG emissions estimation of hydrogen production (grey background indicates methane decomposition systems using natural gas as basis for process energy; electricity from combined cycle power plants (CC) or renewable energy (RE); methane decomposition in molten metal (MM) and thermal gas (TG) system; steam methane reforming (SMR) without or with CO<sub>2</sub> capture and storage (+ CCS)).

**Table 7**  
Variables and indices.

Variables		Indices	
$\eta$	Energetic efficiency	<i>theo</i>	theoretical
$c$	Cost	<i>e</i>	energy
$p$	Annual production	<i>p</i>	Production plant
$WACC$	Weighted average cost of capital	<i>f</i>	Fuel
$GHG$	Greenhouse gas	<i>o&amp;m</i>	Operation and maintenance
		<i>i</i>	Supply route
		<i>ref</i>	Reference technology

be 31 g CO<sub>2</sub>-eq./kWh being between GHG emission for mono-silicon and cadmium telluride systems [66].

## 5.2. Methane supply

Natural gas is considered to be the methane source used for hydrogen production. Average cost for natural gas in UK, Netherlands, Germany, US, and Canada in 2018 are used as a reference with 4.1 €/GJ [67].

Associated GHG emissions of a global average supply chain are comprised of CO<sub>2</sub> emissions e.g. for production, gas upgrading, and transport to the final customer. Additionally, emissions of unburnt methane show a significant impact due a relatively high global warming potential with 30 g CO<sub>2</sub>-eq./g CH<sub>4</sub> in a 100 year and 85 g CO<sub>2</sub>-eq./g CH<sub>4</sub> in a 20 year perspective [61]. For this investigation, CO<sub>2</sub> emissions for the natural gas supply chain are assumed to sum up to 17.2 g CO<sub>2</sub>/MJ<sup>1</sup> considering emissions for natural gas production, long distance transport and distribution in a high pressure system [68]. Average methane leakage is assumed to be 1.7% as estimated for the global natural gas supply [69].

## 5.3. Hydrogen production

Techno-economic parameters of hydrogen production technologies

<sup>1</sup> The central value is the mean of four European supply chains with pipelines transport Russia (7,000 km), Middle East (4,000 km), Norway with CCS technology (1,300 km) and LNG transport [68].

are shown in sections 2.2 and 3. O&M costs are assumed to be 3% and related to the overall investments unless stated differently.

GHG emissions for the manufacturing and commissioning of molten metal reactor system are estimated to be 0.2 kg CO<sub>2</sub>-eq./kg H<sub>2</sub> [70]. Additional GHG emissions for the used molten metal are estimated to be 0.2 kg CO<sub>2</sub>-eq./kg H<sub>2</sub>, reflecting hydrogen production on an industrial scale [70]. Similar -GHG emissions for manufacturing and commissioning of the other chemical processes are assumed. Electrolyser systems show higher values of 0.4 kg CO<sub>2</sub>-eq./kg H<sub>2</sub> [71].

## 5.4. Fuel production based on hydrogen

Substitutes for “classical” conventional fuels can be produced based on hydrogen and carbon carriers (i.e. CO, CO<sub>2</sub>). If these fuel substitutes show similar fuel characteristic as conventional fuels, they can be integrated into the existing energy system without any major changes to infrastructures, supply chains, applications, use behaviour, etc. (i.e. drop in).

Such fuel provision processes are often discussed under the premise that hydrogen is produced by water electrolysis (called power-to-liquid (PtL) or power-to-gas (PtG) processes). However, different hydrogen production routes can also be applied. Thus, two prominent fuel production processes are investigated for the production of

- (1) Synthetic methane (SNG) based on a thermo-catalytic methanation process for substituting natural gas and
- (2) Liquid hydrocarbons based on a Fischer-Tropsch (FT) process for substituting fuels provided from crude oil.

Table 9 shows techno-economic parameters used here for the methanation and Fischer-Tropsch (FT) process, if CO<sub>2</sub> is used as a carbon source.

The CO<sub>2</sub> required as input for the fuel production costs ca. 30 €/t CO<sub>2</sub> reflecting CO<sub>2</sub> e.g. captured from biogas or bioethanol production [6]. Heat integration is not considered between hydrogen production and the subsequent fuel synthesis.

## 6. Results: Hydrogen production

Below, the costs, the GHG emissions, and the CO<sub>2</sub> abatement costs are presented for the various hydrogen production cases. Table 8 provides an overview of the cases and related input parameters representing e.g. world-average natural gas supply chain conditions. Error bars indicate uncertainties in parameters with the hydrogen production technology.

### 6.1. GHG emissions

Fig. 3 shows estimated GHG emissions associated with the considered hydrogen production routes. Four levels of GHG emissions can be distinguished.

- Highest and smallest GHG emissions are related to electrolysis. The electricity source has a paramount impact on the GHG emissions. If low GHG emissions are targeted, hydrogen production in the electrolyser must be powered by a low GHG intensive electricity source. If the electricity source emits 270 g CO<sub>2</sub>-eq./kWh – which is ca. 50% lower than the world average of 520 g CO<sub>2</sub>-eq./kWh [72] – GHG emissions levels of electrolysis hydrogen leads to similar GHG emissions as hydrogen produced in steam methane reforming (SMR).
- The second lowest GHG emissions arise for hydrogen produced from methane decomposition with renewable electricity in plasma systems and steam methane reforming (SMR) including CO<sub>2</sub> capture and storage (CCS). However, GHG emissions can be reduced by 72% maximum compared to steam methane reforming (SMR). Thus,

**Table 8**

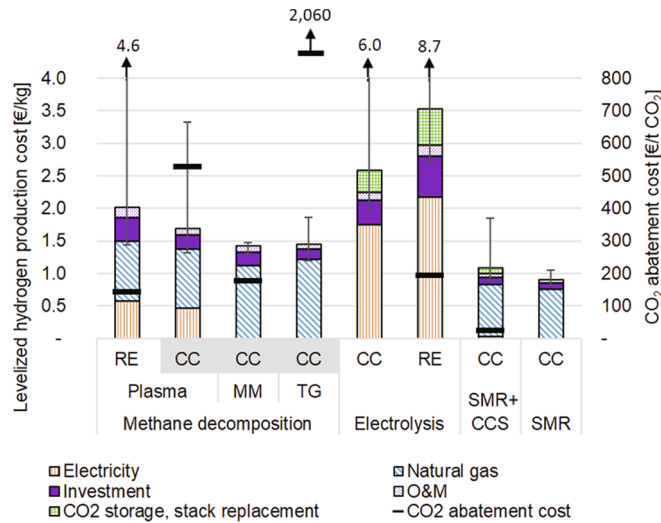
Considered cases for hydrogen production and fuel production (\* indicates that electricity demand is negligible and no additional electricity supply case is considered).

Cases	Hydrogen production	Methane supply	Electricity supply	Fuel production considered for each of the hydrogen production case	Fuel production	
Input parameters	Section 2 and 3	Section 5.2	Section 5.1		Section 5.4	
Results	Section 6				Section 8	
Methane decomposition	Plasma	Global average conditions	Combined cycle gas power plant (CC)		Fischer-Tropsch (liquid fuel production) Reference is fossil crude oil	Catalytic methanation (gas fuel production) Reference is natural gas
	Plasma		Hybrid wind and PV system (RE)			
	Molten metal (MM)		CC*			
	Thermal gas (TG)		CC*			
Alternative hydrogen production	Electrolysis		CC			
	Electrolysis		RE			
production	SMR + CO <sub>2</sub> capture and storage		CC*			
Reference	Steam methane reforming (SMR)		CC*			

**Table 9**

Techno-economic parameters of hydrogen-to-fuel processes using CO<sub>2</sub> as carbon source (based on [6]); equipment cost are related to a plant capacity of 200 MW<sub>fuel</sub>) (brackets indicated bandwidth).

Fuel process	Efficiency (hydrogen to fuel, HHV)	Investment [€/kW <sub>fuel</sub> ]	Annual O&M cost related to investment
Catalytic methanation (natural gas substitute)	72% (66%-78%)	195 (29–293)	4%
Fischer-Tropsch (FT) fuels (crude oil substitute)	65% (56%-74%)	412 (309–721)	



**Fig. 4.** Levelized hydrogen production cost and CO<sub>2</sub> abatement cost (reference is steam methane reforming; grey background indicates methane decomposition systems using natural gas as basis for process energy electricity from combined cycle power plants (CC) or renewable energy (RE); methane decomposition in molten metal (MM) and thermal gas (TG) system; steam methane reforming (SMR) without or with CO<sub>2</sub> capture and storage (+ CCS)).

above 28% of the GHG emissions are still emitted and longer term GHG reduction targets (e.g. global GHG neutrality according to the Paris Agreement by 2050 [73]) cannot be achieved.

- GHG emissions of hydrogen from steam methane reforming (SMR) and remaining methane decomposition system configurations are in a range between 11 and 14 kg CO<sub>2</sub>-eq./kg H<sub>2</sub>. Thus, these methane decomposition systems show only a small benefit in GHG emission reductions. I.e. they should not be introduced globally from a climate change perspective.

GHG emissions of hydrogen produced in plasma methane decomposition systems and in electrolyzers are substantially lower if electricity from renewable sources is used. The released GHG caused by the respective technology is determined by the electricity source. Thus, modifying the electricity source allows for a change to the GHG emissions of these technologies still in the aftermath.

Substantial GHG emissions arise also from the overall supply chain of the natural gas contributing up to 96% of the hydrogen related GHG emissions. These GHG cannot be prevented through the use of methane decomposition systems or CO<sub>2</sub> capture and storage (CCS). They can only be reduced if the GHG emissions would be decreased throughout the overall natural gas supply chain (section 7.1).

## 6.2. Production and CO<sub>2</sub> abatement cost

Fig. 4 shows the levelized production and CO<sub>2</sub> abatement costs of hydrogen produced by the different systems. Thus, no clear pattern exists between hydrogen costs, GHG emissions, and CO<sub>2</sub> abatement costs.

The highest costs are related to the lowest GHG emissions of hydrogen (electrolysis powered with renewable energy). However, the lowest cost of hydrogen with reduced GHG emissions is also associated with low levels of GHG emissions (steam methane reforming (SMR) with CO<sub>2</sub> capture and storage (CCS)). Applying CCS to SMR increase the costs by only 20% and result with the lowest CO<sub>2</sub> abatement costs of 24 €/t CO<sub>2</sub>-eq. However, a higher uncertainty exists in the parameters of the steam methane reforming (SMR) process with CO<sub>2</sub> capture as the error bars indicate. Even higher hydrogen costs than in methane decomposition systems are within the uncertainty range. Furthermore, CO<sub>2</sub> transport and long-term CO<sub>2</sub> storage costs of 10 €/t CO<sub>2</sub>-eq. are considered here characterised by high uncertainties (i.e. they could be higher than 20 €/t CO<sub>2</sub>-eq. [7]).

Systems with a substantial electricity demand (i.e. plasma methane decomposition and electrolysis) lead to the highest hydrogen provision costs. The total energy demand, including electricity and natural gas, of plasma systems is similar to the other methane decomposition systems

and thus not attributed to the higher hydrogen costs. Electrolysis systems consume ca. 30% less energy than methane decomposition systems and roughly the same energy as steam methane reforming (SMR) concepts. But electricity is characterized by 128 to 183% higher costs compared to natural gas. Additionally, electricity produced from renewable energy shows a lower availability and thus leads to a lower capacity factor for the hydrogen production system and thus additionally higher costs<sup>2</sup>. Therefore, systems with a substantial electricity demand can produce hydrogen only at similar costs, if the costs of electricity from renewable energies decrease to a level of the natural gas prices.

The methane decomposition systems show substantial differences in the CO<sub>2</sub> abatement costs (141 to 2,060 €/t CO<sub>2</sub>-eq.) although hydrogen costs and GHG emissions are in a similar range. The high sensitivity of the CO<sub>2</sub> abatement costs can partly be explained by the marginal difference in GHG emissions compared to the reference production system. The thermal gas methane decomposition systems produce hydrogen with only 2% lower GHG emissions than the steam methane reforming process (SMR).

## 7. Sensitivity analysis: Hydrogen production

The sensitivity analysis investigates the impact of different boundary conditions. It reflects the performance of the hydrogen production technologies, e.g., under different regional circumstances.

### 7.1. GHG emissions

The GHG emissions of the natural gas supply chain have a strong impact on the GHG emissions of the considered hydrogen production (Fig. 6). Methane decomposition systems, and especially plasma systems powered by electricity from renewable sources of energy, show the strongest relation because the GHG emissions from the natural gas supply chain are the major source of the overall GHG emissions. The effect of the supply chain is lower for steam methane reforming (SMR) as combustion related emissions play a stronger role.

Thus, if the natural gas GHG supply chain emissions are lower than global average conditions (base case), the GHG emissions of methane decomposition decrease more compared to steam methane reforming and vice versa. For example, under European supply chain conditions (10.1 and 17.0 g CO<sub>2</sub>-eq./MJ [74]), the plasma methane decomposition using electricity from renewables (RE) produces hydrogen with 67 to 77% lower GHG emissions than steam methane reforming. Under global conditions the GHG emissions are only 55% lower. Thus, the strong dependency of the natural gas supply chain has to be considered if hydrogen is to be traded internationally. The choice of a natural gas resource with low GHG emissions (i.e. the choice of an exporting country) can show a strong effect on the hydrogen GHG emissions and can outweigh the choice of hydrogen production technology.

However, the sequence of technologies remains the same in terms of GHG emissions for a broad range of natural gas supply chain GHG emissions. But above ca. 27 g CO<sub>2</sub>/MJ emissions from the supply chain, methane decomposition systems using natural gas as process energy source, could lead to higher GHG emissions than steam methane reforming. At very low supply chain GHG emissions, the plasma methane decomposition powered by electricity from renewables allows very low GHG emission levels similar to electrolysis powered by renewable electricity. However, such low supply chain emissions occur only in a very limited number of cases. Furthermore, current research indicates that supply chain emissions especially caused by methane leakages are underestimated [75,76].

<sup>2</sup> Underlying cost for electricity produced in combined cycle power plants result to 33.6 €/MWh compared to 41.7 €/MWh from a combined PV and wind system.

Here, GHG emissions are assessed under a 100-year global warming potential (GWP). But this assumption does not show a higher validity in estimating the impact on global warming than using other time frames [61]. For example, a 20-year GWP emphasizes the short-term effects on the climate. As methane leakages are one major share in natural gas supply chain GHG emissions, global average supply chain emissions increase by 65% under a 20-year GWP (Fig. 5).

### 7.2. Production and CO<sub>2</sub> abatement cost

Hydrogen production costs show a strong dependency on the energy costs (Fig. 6). The energy costs make >62% of the overall costs for all technologies. The relation is stronger if the share of energy costs is higher. But energy costs are only one cost driver and investments can be another. Changes in the weighted average cost of capital lead to stronger changes in hydrogen production costs for systems showing higher investment demand, i.e. the electrolysis option and all systems using electricity from renewable source of energy because they are characterized by high initial investments. Additionally, systems using electricity from renewable sources show a higher dependency due to a lower utilization of the system (lower capacity factor) and thus a higher impact of investments.

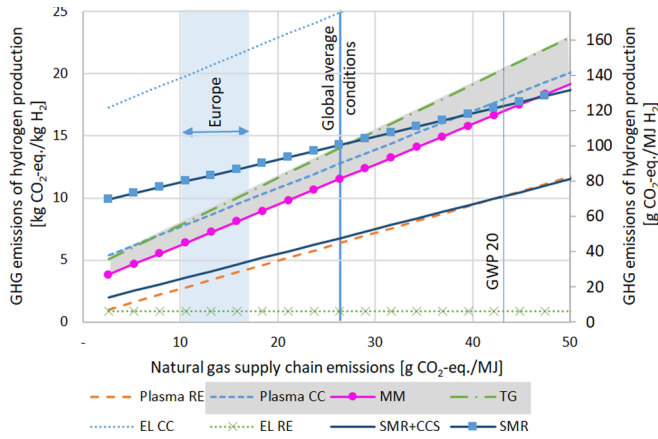
### 7.3. Excursus: Impact of carbon black production

The methane decomposition yields solid carbon as a by-product. If this is considered as a marketable product, it can significantly impact cost and the GHG emissions of hydrogen production [7,9,13,16]. Depending on the process characteristics carbon is produced with different structures [13]. Carbon black shows the largest global demand from these various carbon products. Over 90% of the global carbon black produced, so far, is used in tires and other rubber products as reinforcing fill – among others – increasing the abrasion resistance of the product [16]. The market size of carbon black today is ca. 16.4 Mt/a [7]. The production of this amount of carbon black and solid carbon by methane decomposition systems corresponds to a hydrogen production of 5.5 Mt/a being 7% of the global hydrogen demand (73 Mt/a in 2018 [77]). Due to these market relations, the calculations presented above do not consider solid carbon as marketable side product.

For an application in smaller quantities or (e.g.) for the first methane decomposition systems, carbon credits and returns through marketing of carbon black could be considered. Currently, carbon black is mostly produced from heavy crude oil fractions processing in the furnace black and oil-furnace process. This processes also yields hydrogen typically used for providing heat for the process as well as externally [16]. The production leads to GHG emissions of 2.62 kg CO<sub>2</sub>-eq./kg carbon black [78]. These production-related GHG emissions could be avoided if carbon black from methane decomposition would be used instead. Substantial emissions saving in the range of 8 kg CO<sub>2</sub>-eq./kg hydrogen could be attributed. However, a detailed life-cycle analysis considering the consequences of the implementation is necessary in order to account e.g. for substitution effects.

Prices for carbon products range from 400 to 2,000 €/t for carbon black itself and significantly higher prices of > 1,000,000 €/t can be achieved for high grade special carbon products [13]. Fig. 7 shows that for a carbon black revenue between 500 and 750 €/t hydrogen by methane decomposition systems can be produced at zero cost. This explains why commercialisation projects target carbon black production so far (Table 2).

It seems possible that low cost carbon from methane decomposition systems could find new applications, such as, in construction materials, replacing metallurgical coke in steel production, or as soil amendment [13,14]. This means an additional demand for solid carbon that would possibly not be created without the methane decomposition process and thus no carbon credit would apply. Furthermore, it is necessary to



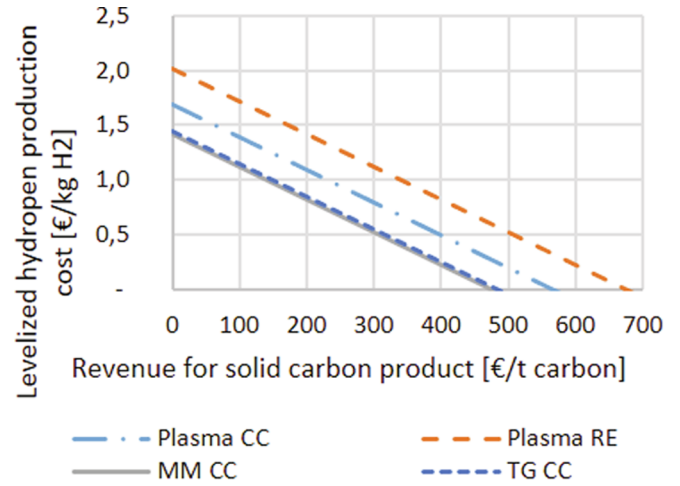
**Fig. 5.** GHG emissions of hydrogen production vs. natural gas supply GHG emissions (grey area indicates bandwidth of methane decomposition systems using natural gas as a process energy; global warming potential (GWP, 100 year is default); electricity from combined cycle power plants (CC) or renewable energy (RE); methane decomposition in molten metal (MM) and thermal gas (TG) system; steam methane reforming (SMR) without or with CO<sub>2</sub> capture and storage (+ CCS)).

investigate if this new application leads to long-term storage of the carbon or if it would be released to the atmosphere as CO<sub>2</sub> after some time.

## 8. Results: Fuel production based on hydrogen

Fig. 8 and Fig. 9 show GHG emissions and production costs of liquid fuel (e.g. gasoline, Diesel, kerosene) and methane each derived from hydrogen. The sizes of the bubbles represent the standard deviation (i.e. they indicate uncertainties in the techno-economic assumptions). The synthesized liquid and gaseous fuels are compared against the properties of conventional fuels. For liquid fuels well-to-wheels GHG emissions of 89 g CO<sub>2</sub>-eq./MJ<sub>HV</sub> (94.1 g CO<sub>2</sub>-eq./MJ<sub>LHV</sub> according to EU Fuel Quality Directive) and a crude oil price of 10 €/GJ (2018, [67]) are considered. The same assumptions from section 5.2 for natural gas are applied.

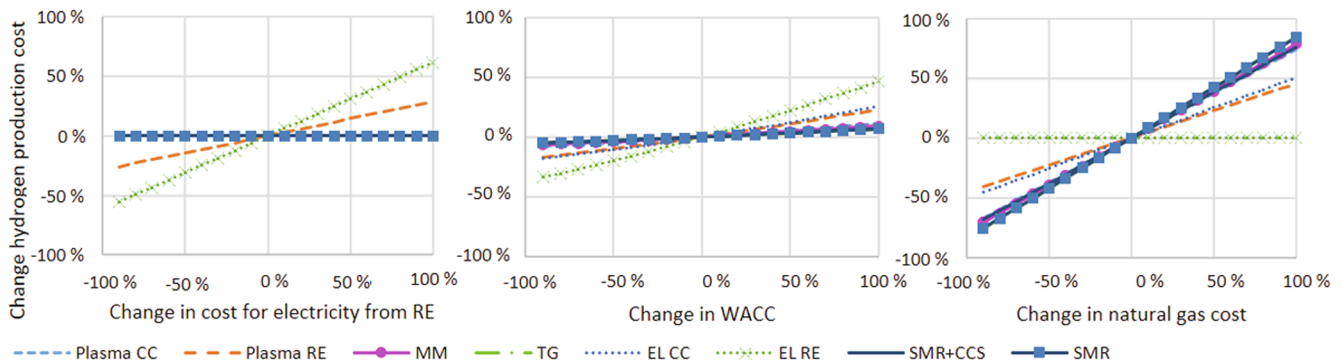
Only three hydrogen supply routes lead to synthesized liquid or gaseous fuels associated with lower GHG emission than the fossil reference. And, only hydrogen from electrolysis powered by electricity



**Fig. 7.** Hydrogen production cost as function of solid carbon revenue.

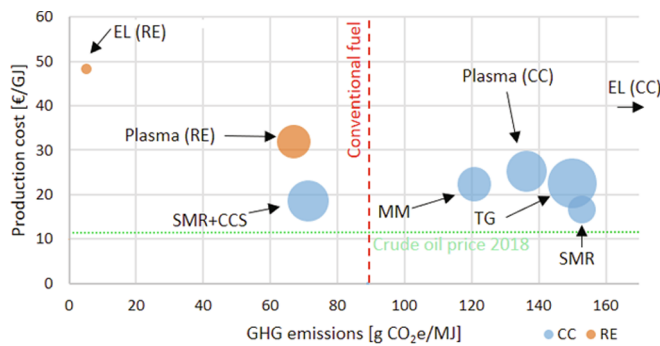
from renewables leads to substantially lower GHG emissions (-94%). Plasma methane decomposition powered with renewable energy and steam methane reforming (SMR), including CO<sub>2</sub> capture and storage (CCS), achieve only 16 to 25% lower GHG emissions than the fossil reference. The remaining hydrogen supply routes lead to even higher GHG emissions. Thus, only electrolysis powered with electricity from wind and/or solar energy allows the synthesizing of fuel that can be applied to meet the given long-term global warming mitigation goals.

Fuel synthesis based on plasma methane decomposition leads to similar GHG emissions, but higher costs than steam methane reforming (SMR) with CO<sub>2</sub> capture and storage (CCS). Thus, methane decomposition systems do not show a benefit under global circumstances. The CO<sub>2</sub> abatement costs of fuel synthesis based on electrolysis with renewable energy and on steam methane reforming (SMR), including CO<sub>2</sub> capture and storage (CCS), are similar for liquid fuels (457 and 485 €/t CO<sub>2</sub>-eq.). Thus, higher GHG emission reductions through the electrolyser system compensates for higher hydrogen costs. For methane synthesis, the lower GHG emission using electrolysis outweighs the higher costs compared to SMR with CCS. CO<sub>2</sub> abatement costs of 508 €/t CO<sub>2</sub>-eq. result if electrolysis produces hydrogen compared to 916 €/t CO<sub>2</sub>-eq. for SMR with CCS.

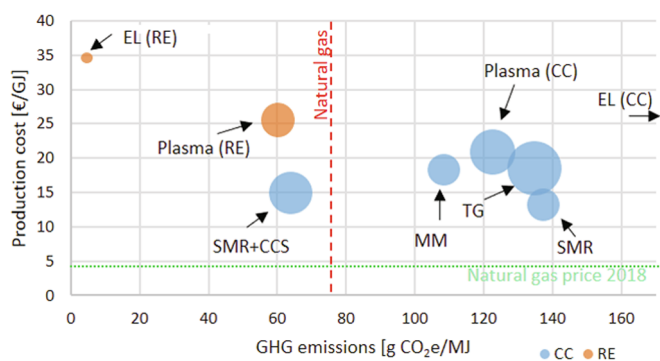


**Fig. 6.** Sensitivity analysis regarding changes in the economic boundary conditions (electricity from combined cycle power plants (CC) or renewable energy (RE); methane decomposition in molten metal (MM) and thermal gas (TG) system; electrolysis (EL); steam methane reforming (SMR) without or with CO<sub>2</sub> capture and storage (+ CCS)).





**Fig. 8.** GHG emissions and cost of liquid fuel production through Fischer-Tropsch process depending on hydrogen production route (EL: electrolysis, methane decomposition with MM: molten metal and TG: thermal gas reactor, SMR: steam methane reforming, CCS: CO<sub>2</sub> capture and storage).



**Fig. 9.** GHG emissions and cost of methane production through catalytic methanation process depending on hydrogen production route (EL: electrolysis, methane decomposition with MM: molten metal and TG: thermal gas reactor, SMR: steam methane reforming, CCS: CO<sub>2</sub> capture and storage).

## 9. Final considerations

Hydrogen can be produced through methane decomposition yielding hydrogen and solid carbon. Different technological approaches exist and three process configurations are assessed here (plasma, molten metal, and a thermal gas reactor system) regarding life-cycle GHG emissions and the levelized hydrogen production costs. These systems are compared to electrolysis and steam methane reforming (SMR) with and without CO<sub>2</sub> capture and storage (CCS).

The assumptions about the supply chain GHG emissions determine the absolute performance of the methane decomposition configurations, because the supply chain emissions account for >65% of the hydrogen related GHG emissions under global average supply chain conditions. However, the relative performance of methane decomposition systems is robust and the GHG emissions for providing the process energy are the key factor. Accordingly, plasma-based methane decomposition systems using electricity from renewable sources (i.e. the process energy is provided with (very) low GHG emissions) produce hydrogen with significantly lower GHG emissions than the other methane decomposition configurations. Combusting natural gas for providing the process heat, as in the molten metal and thermal gas configurations, releases relative higher GHG emissions due to the natural gas supply chain and additionally through combustion. Furthermore, these configurations show a higher heat demand compared to the plasma system. Under the global average natural gas supply chain conditions, the GHG emissions caused by the plasma systems are 45 to 55% lower.

The GHG emissions of the process heat for the methane decomposition systems also determine the GHG emission performance compared to electrolysis and steam methane reforming (SMR). However, the supply chain emissions affect the GHG emissions of the different hydrogen production pathways to varying degrees. Therefore, the boundary conditions can change the relative performance. Under global average natural gas supply chain GHG emissions, systems producing heat by combustion of natural gas produce hydrogen with similar GHG emissions as the “classical” steam methane reforming (SMR). Under these boundary conditions, they are not a viable alternative hydrogen production technology from a climate protection perspective. Still, the plasma-based methane decomposition system using renewable electricity emit similar low GHG compared to steam methane reforming with CO<sub>2</sub> capture and storage. The situation changes if lower than global average GHG supply chain emissions are assumed. For example, in a European gas supply, the methane decomposition configurations using fossil energies for the process heat can produce hydrogen with 20 to 45% lower GHG emissions than steam methane reforming (SMR).

More realistic estimations of GHG emissions are potentially made when considering higher GHG supply chain emissions. Latest research indicates that global GHG emissions (i.e. emissions of unburnt methane) released throughout the overall provision of natural gas are underestimated [76]. Real methane emissions of the oil and gas industry exceed estimated emissions by 60% in the US [75]. Furthermore, natural gas from unconventional sources (such as shale gas) is likely to lead to substantially higher emissions [79]. Furthermore, it seems unlikely that supply chain emissions decrease substantially because powerful mechanisms are not in place aiming at the reduction of the supply chain emissions specifically.

Only hydrogen production by electrolysis powered by electricity from renewable energy sources is independent of the natural gas supply chain and leads to (very) low overall GHG emissions. Furthermore, this is the only hydrogen production route that allows for the synthesizing of fuels (methane or gasoline / diesel / kerosene equivalents) with low GHG emission levels. The other hydrogen production routes lead to life-cycle GHG emissions similar or even higher than the fossil energy carriers (i.e. the current situation).

The hydrogen production costs are reversely affected by the energy source used to provide the process heat of methane decomposition systems. The plasma methane decomposition process produces hydrogen at higher costs than the methane decomposition systems that combust natural gas. However, under global average supply chain conditions, the lower GHG emissions outweigh higher costs so that the plasma-based system using renewable electricity produce hydrogen with lower CO<sub>2</sub> abatement costs (141 €/t CO<sub>2</sub>-eq.). However, steam methane reforming with CO<sub>2</sub> capture and storage produce hydrogen at similar GHG emissions levels as the plasma system, but the costs are significantly lower and so are the CO<sub>2</sub> abatement costs.

Under the given assumption of a global natural gas supply chain, the methane decomposition systems do not show cost or GHG emission benefits. However, receiving a revenue for the produced carbon could change the hydrogen production costs significantly. Already at moderate carbon prices, the hydrogen production costs can be very low. As the current market size of carbon black is too small for large scale application of methane decomposition processes for hydrogen production (7% of global hydrogen demand), a small-scale application of this process is conceivable.

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## CRediT authorship contribution statement

**Sebastian Timmerberg:** Conceptualization, Methodology, - Investigation, Writing - original draft, Writing - review & editing. **Martin Kaltschmitt:** Resources, Funding acquisition, Writing - review & editing. **Matthias Finkbeiner:** Supervision.

## 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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