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A comparison of the most promising low-carbon hydrogen production technologies

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A B S T R A C T

The energy transition to be successful requires an increasing share of renewable electricity and large amounts of low-carbon hydrogen. This paper presents a comparison of the following promising low-carbon hydrogen production technologies. Typical electrolyzer technologies, namely alkaline electrolysis (AEL), polymer electrolyte membrane electrolysis (PEMEL), and high-temperature electrolysis (HTEL), as well as methane pyrolysis systems based on thermal, plasma and catalytic decomposition along with steam methane reforming (SMR) with carbon capture utilization or storage (CCUS) are discussed and evaluated. These hydrogen technologies are then compared on the basis of assessment criteria such as the technology readiness level (TRL), scalability, levelized cost of hydrogen (LCOH), the impact of by-products and their carbon footprint. Compared to the other two low-carbon hydrogen production technologies mentioned in this paper, methane pyrolysis performed well and was found to be a promising alternative. Using exclusively renewable electricity for the required process heat yields lower CO_2 emissions than currently operating SMR-CCUS systems can achieve and shows competitive LCOH. Moreover, in the course of decarbonization and due to its inadequate CO_2 capture rates, the SMR-CCS technology should serve exclusively as an interim solution to the rapid market ramp-up of the low-carbon hydrogen economy. With respect to the ambitious green hydrogen targets, it was determined that electrolysis is indispensable, but still needs to be scaled up as it currently does not produce sufficient amounts of hydrogen. Furthermore, the LCOH of methane pyrolysis was lower than the one of electrolysis using renewable electricity. Therefore, methane decomposition is considered a promising low-carbon hydrogen production technology that needs to be implemented alongside green and blue hydrogen to contribute to a successful energy transition.

1. Introduction

Mastering the energy transition is an urgent and challenging mission nowadays. Global greenhouse gas (GHG) emissions must be massively reduced in the decades ahead to achieve the 2 °C targets. The impacts of global warming of 1.5 °C above pre-industrial levels are shown by the Intergovernmental Panel on Climate Change (IPCC): A further rise in global temperatures will have long-lasting and partly irreversible consequences, the intensity and frequency of extreme weather events will increase and a reduction in anthropogenic GHG emissions is urgently required [1]. For the agreed targets to be met, GHG emissions must be reduced to zero by 2050.

In 2019, two thirds of global GHG emissions were caused by energy-related CO_2 emissions [2]. The essential step towards a climate-neutral energy system is the steady and significant increase of renewable energy (RE). In 2020, the share of RE in global electricity production was 29 %, and the International Energy Agency (IEA) expects a further increase in the coming years [3]. With the growing share of RE, the increasing amounts of fluctuating electricity fed into the grid result in the curtailment of RE systems, not realizing its full potential. In order to stabilize the power grid and, above all, to be able to use the total share of renewable electricity generated, besides batteries, other storage technologies must be established and used at a higher pace than ever before.

However, for the decarbonization of the entire energy system to be successful, large amounts of climate-neutral hydrogen are necessary, to be produced efficiently and as cost-effective as possible, since its use does not cause direct CO_2 emissions. Legislation such as the European Green Deal, in which clean hydrogen is anchored, and international studies like the IEA's "World Energy Outlook 2021" underline its steadily growing importance and assume that hydrogen is essential for a GHG-neutral energy future [4,5]. Hydrogen offers the possibility of storing the increasing, fluctuating share of renewable electricity over long periods, rendering the energy transportable and flexible to use

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Nomenclature

AEL	alkaline electrolysis
CB	carbon black
CCS	carbon capture and storage
CCU	carbon capture and utilization
CCUS	carbon capture utilization or storage
EOR	enhanced oil recovery
GHG	greenhouse gas
HTEL	high temperature electrolysis
LCOH	levelized cost of hydrogen
LHV	lower heating value
PEMEL	polymer electrolyte membrane electrolysis
PSA	pressure swing adsorption
RE	renewable energy
rSOC	reversible solid oxide cell
SMR	steam methane reforming
TRL	technology readiness level
WGS	Water-gas-shift

across different sectors. Furthermore, not only the potential of hydrogen to compensate for the seasonal fluctuations of RE sources should be addressed, but also the opportunity to decarbonize sectors such as the steel or chemical industry, where it has been difficult to reduce CO_2 emissions so far. In addition, hydrogen also has excellent potential as an energy carrier since either in pure or in bound form, e. g., as ammonia, no direct CO_2 is released. Because of its wide range of applications, low-carbon hydrogen is regarded as an essential part of the future energy system.

In the course of climate change mitigation, green hydrogen – water electrolysis powered by electricity from RE – is becoming increasingly more important in the production of climate-neutral hydrogen. It is seen as an indispensable technology that needs to be implemented as a long-term solution. However, additional low-carbon technologies have to be taken into account to achieve the intended climate goals. Another option is decarbonizing steam methane reforming (SMR) – the currently prevailing hydrogen production process (grey hydrogen) – by combining it with carbon capture and storage (CCS) or utilization (CCU), to produce so-called blue hydrogen. Turquoise hydrogen is also considered a promising low-carbon hydrogen production option since no CO_2 is released during the methane pyrolysis process.

As the need for low-carbon hydrogen keeps rising, this paper assesses the following promising technologies with the main focus on methane pyrolysis: The typical electrolysis technologies – AEL, PEMEL and HTEL – are addressed, as well as SMR-CCS and methane pyrolysis based on plasma, thermal, and catalytic pyrolysis.

Most of the studies found in the literature either focus only on one pyrolysis technology compared to electrolysis or SMR [6–9]. Others only compare the methane pyrolysis variants with each other [10,11] and still others focus on the costs or GHG emissions of low-carbon hydrogen technologies [4,12–14]. Since methane pyrolysis is rarely mentioned compared to green and blue hydrogen, or has so far only been mentioned as a niche application, this paper is intended to offer an all-encompassing comparison: What are the key characteristic differences between methane pyrolysis methods and water electrolysis as well as SMR with CCS? How significant is the potential of methane pyrolysis for low-carbon hydrogen production compared to electrolysis or SMR with CCS, and is it a potential alternative technology for the production of low-carbon hydrogen?

This article is structured as follows: To be able to evaluate these various processes and compare them, a literature review on the basics of these considered technologies is presented in Section 2, containing a more detailed description of methane pyrolysis which is, as of today, the least established technology option among the ones considered in this paper. Section 3 compares the various technologies based on assessment criteria such as scalability, technology readiness level (TRL) and economic as well as ecological aspects. Moreover, it is discussed to what extent the use of by-products such as solid carbon from methane pyrolysis can increase the overall efficiency. This holistic comparison intends to evaluate which technologies can prevail and thus contribute to a successful energy transition. The results are presented and discussed in Section 4 and, finally, the most important findings are summarized in Section 5.

2. Technologies for the production of low-carbon hydrogen

Hydrogen is currently mainly produced from fossil fuels and, with a share of only <1 % of this amount, electrolysis and SMR-CCS both play a subordinate role so far [14]. To reach the climate goals, set in the Paris Agreement, these low-carbon technologies are expected to increase on a large scale. In the following, the principles of these three competing low-carbon hydrogen production technologies are described.

2.1. Electrolysis

Since the splitting of water produces only oxygen as a by-product, water electrolysis is currently one of the most promising processes for the production of climate-neutral hydrogen. The decomposition of water into oxygen and hydrogen by means of electrical energy was discovered in 1800 [15] and a first large-scale electrolyzer with a capacity of 27,900 $Nm^3\ h^{-1}$ was installed in Norway as early as 1929 [16]. With the establishment of natural gas, the importance of electrolysis for hydrogen production declined and the more cost-effective SMR has prevailed until today [14]. However, as no direct CO_2 is emitted, water electrolysis is being targeted again in the course of the energy transition. To produce green hydrogen, the energy required for the endothermic water-split reaction

$$H_2O \rightarrow H_2 + 0.5\ O_2 \qquad \Delta_R H^\circ = 285.83\ kJ\ mol^{-1} \tag{1}$$

needs to be provided from RE sources.

Water electrolysis can be divided into the following three basic principles, which mainly differ in the electrolyte used: AEL, PEMEL and HTEL. These types of electrolyzers are briefly explained below in order to understand the advantages and disadvantages of each technology, presented in Fig. 1, as well as the differences to the other low–carbon hydrogen production processes. The main technical parameters are summarized in Table 1.

Today, the most common and mature technology is the **AEL**. The current densities are rather low (0.2–0.6 A cm^{-2}) and the efficiency is between 63 and 70 % (based on the lower heating value (LHV)) [13,14,17,18]. Currently, modules with capacities ranging from several hundred to 1,200 $Nm^3\ h^{-1}$ can be purchased from various manufacturers [18–20] and todays commercial AEL systems reach an electrical output of up to 25 MW, which is achieved by the largest AEL currently in operation – the Cachimayo plant in Peru [21]. This technology does not require any expensive or rare catalyst materials and has proven to have a long lifetime, making the AEL very cost-efficient. Compared to other electrolyzer types, the complexity is higher due to the necessary potassium hydroxide cycle and its corrosive behavior [17].

In contrast to the AEL, the more recent **PEMEL** technology shows extremely high dynamics and is therefore well compatible with the fluctuating power feed from RE. With its fast system response in the millisecond to second range – from standby to full power – it is ideally suited for green hydrogen production and an important water electrolysis technology for the decarbonization [17,18,22]. The PEMEL uses a solid electrolyte, a polymer membrane, and has seen a lot of R&D activities in recent years. So far it has also reached the MW output range, with the world's largest PEMEL plant (20 MW), operated by Air Liquide

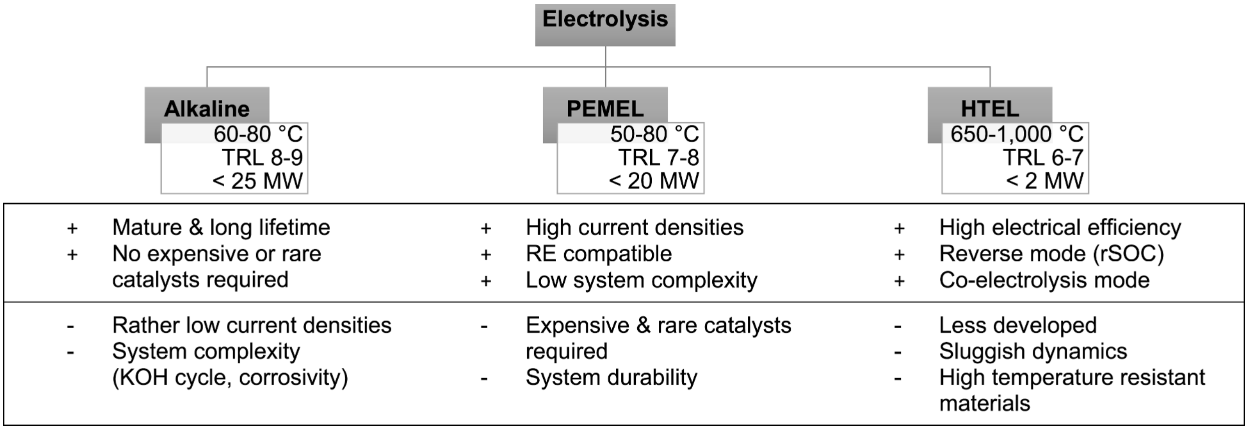

Fig. 1. Comparison of the advantages and disadvantages of the electrolysis technologies AEL, PEMEL and HTEL.

Table 1
Technical parameters of AEL, PEMEL and HTEL.

	AEL	PEMEL	HTEL	
TRL [–]	8–9	7–8	6–7	[13,19]
System efficiency (LHV) [%]	63–70	56–65	74–84	[13,14,17,18]
Current density [A cm^{-2}]	0.2–0.6	0.6–3.0	0.3–1.0	[14,17,18]
Operating temperature [°C]	60–80	50–80	650–1,000	[14,17,18]
System size [MW]	Up to 25	Up to 20	Up to 2	[21]
Electricity consumption [kWh Nm^{-3}]	4.3–4.8	4.6–5.3	3.6–4.0	[13,14,17,18]

since the beginning of 2021 [23]. Even though the efficiencies of 56–65 % are lower compared to those of AEL, this technology has significantly higher current densities of up to 3 A cm^{-2} [14,17,18]. The PEMEL needs further development to increase the system durability and to lower costs, as rare and expensive materials such as Iridium or Platinum are required.

The least mature electrolyzer in this comparison is the **HTEL**. As a high-temperature heat source (650–1000 °C) is used and steam (instead of water) is split, less electricity (3.6–4.0 kWh Nm^{-3}) is needed producing the same amount of hydrogen compared to low temperature electrolyzers (4.3–5.3 kWh Nm^{-3}). This makes the HTEL the electrolyzer technology with the highest electrical efficiency of 74 to 84 % [13,14,17,18]. Due to the high temperatures, HTEL is particularly suitable in combination with processes in the steel or chemical industry with their available high-temperature heat streams. An outstanding advantage of the HTEL is its reverse mode – reversible solid oxide cell (rSOC), in which switching between electrolysis and fuel cell mode is possible providing grid balancing services. Furthermore, it can also be operated in co-electrolysis mode using CO_2 producing, e. g., hydrocarbons [14,17]. At present, TRL is in the range 6–7 and due its sluggish dynamics [13], the HTEL still needs further R&D. Especially as electrical outputs of only up to 2.4 MW have been achieved so far [21,24]. In addition, high temperature resistant materials required are expensive and can lead to manufacturing problems.

To give an overview of the hydrogen capacity range achieved so far by electrolysis, Table 2 summarizes the main large-scale electrolyzers realized to date. For details the reader is referred to the references given in this Table. It can be summarized that PEMEL systems are preferably combined with RE from wind or PV due to the possible high dynamics and its quick-start capability [18,22], whereas AEL and especially HTEL systems need longer start-up times and are more suitable for stationary operation in industrial applications. Even if the AEL and PEMEL have a TRL of 9 and 8 [19], all three electrolysis technologies are subject to constant further development (efficiencies, materials, costs etc.) to advance their performance and range of application for a successful energy transition.

2.2. *Steam methane reforming with CCUS*

Today, the world's leading technology for hydrogen production is SMR [29]. In the light of decarbonization efforts this technology with CO_2 emissions from 9 to 11 $kg_{CO_2}\,kg_{H_2}^{-1}$ is no longer acceptable, although it is currently the most cost-efficient one [2,14]. Converting this GHG-intensive process into a low-carbon one by augmenting it with a CCS system holds great potential for the medium-term preservation of the SMR technology. This blue hydrogen could be indispensable as an interim solution for a rapid market ramp-up of a low-carbon hydrogen economy. In its "Hydrogen Decarbonization Pathways", the Hydrogen

Table 2
Overview of selected large-scale electrolyzers.

Project (Country)	Capacity [Nm^3 h^{-1}]	Power [MW]	Module count	Commissioning	Additional information	
Aswan-Dam (Egypt)	32,400	156	132	1970	AEL, out of operation since 2019	[15,16,25]
Glomfjord (Norway)	27,900	142	150	1929	AEL, out of operation since 1971	[16]
Cachimayo (Peru)	4,700	25	7	1962	World's largest electrolyzer, AEL	[16,21]
FH2R (Japan)	1,200	10	1	2020	World's largest single-stack AEL	[20,21]
Air Liquide (Canada)	3,800	20	4	2021	World's largest PEMEL	[21,23,26]
REFHYNE (Germany)	1,650	10	5	2021	Europe's largest PEMEL	[27]
MultiPLHY (Netherlands)	670	2	12	2021	World's largest HTEL	[24,28]

Table 3
Overview of selected SMR-CCS projects.

Project (Country)	Capacity [$Nm^3\ h^{-1}$]	SMR units	Capture rate [%]	Commis-sioning	Additional information	
Quest (Canada)	420,000	3	47	2015	Capturing 79 $\%_{CO2}$ from the synthesis gas; saline aquifers	[31,32,36]
Port Arthur (USA)	240,000	2	54	2013	Capturing 90 $\%_{CO2}$ from the synthesis gas; EOR	[31,32,37,38]
Port-Jérôme (France)	50,000	1	< 37	2015	Capturing CO_2 from 2/3 of the PSA tail gas; CCU	[39,40]
Tomakomai (Japan)	n. a.	1	< 55	2016	Capturing 99,9$\%_{CO2}$ from a portion of the PSA tail gas; offshore sandstone reservoirs	[40–42]

Council states that a mixture of blue and green hydrogen will be necessary in order to be able to cover the future hydrogen demand, since a strict pursuit of exclusively a “green scenario” would be associated with various scale-up problems [30].

The reaction of natural gas with steam takes place in two steps, which form the following endothermic overall reaction:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \Delta_R H^{\circ} = 165.12\ kJ\ mol^{-1} \tag{2}$$

The required heat input for the reactor is generated by burning additional natural gas together with the tail gas from the pressure swing adsorption (PSA), resulting in the above mentioned high GHG emissions [31].

CO_2 can be separated from three parts of the SMR process causing different capture rates: (i) From the synthesis gas after the water–gas-shift-(WGS)-reaction (up to 60 %), (ii) from the tail gas leaving the PSA (up to 55 %) and (iii) from the flue gas of the reformer combined with capturing from the synthesis gas (up to 90 %) [14,32,33]. Due to the fact that the gas mixture downstream of the WGS is already under high pressure, the separation from the synthesis gas is the technically simplest method.

Kearns et al. estimate the global CO_2 storage capacity available to be between 2,400 to 16,500 Gt_{CO2}, excluding capture options that are difficult to access [34]. In comparison, global CO_2 emissions have been 31,5Gt_{CO2} in 2020 and the ones for global hydrogen production from fossil fuels close to 0,9 Mt_{CO2} [3,13,21]. Even if sufficient storage capacity is available, sequestration of CO_2 is controversial worldwide, partly because of potential leakage from storage sites. In this light, CCU, e. g., for the production of synthetic fuels is to be preferred.

Another important point to consider with SMR-CCS is that a CCS unit has a negative impact on the efficiency of the SMR plant: Khojasteh et al. found that a CCS expansion with a capture rate of 90 % increases the natural gas consumption of an SMR plant by 39 % and decreases the efficiency by up to 18 $\%_{LHV}$ [35].

Combining SMR with CCS is currently only used as a niche application [2]. According to the Global CCS Institute, today, four commercial SMR-CCS systems are in operation worldwide (s. Table 3) and further 15 are expected to come online by 2028 [32,43]. Due to a study regarding the technological readiness of CCS systems, SMR-CCS systems have been operated as a mature technology over years, like the Port Arthur plant with a TRL of 9 [32]. For details about today’s operational projects the reader is referred to the references given in Table 3.

It can be summarized that in today’s plants only the CO_2 resulting from the process chemistry is captured, although a further 40 % of the CO_2 generated is present in the reformer flue gas due to the energy supply. For example, a study regarding the Quest plant in Canada showed that in 2019 nearly 79 % of the CO_2 contained in the synthesis gas was captured [36]. However, as only the CO_2 from the synthesis gas – containing approx. 60 % of the total CO_2 produced [33] – is separated, an overall system capture rate of 47 % can be calculated. Thus, the capture rates achieved so far are only 37–54 % and further R&D is necessary. For the future, IRENA expects CO_2 capture rates of 85–95 % through further improvement, while according to IEAGHG capture rates of up to 96 % are possible [2,33]. Despite this possible progress, it must be taken into account that such future SMR-CCS plants will nevertheless emit 4–15 % of the resulting CO_2 and blue hydrogen will thus not be climate-neutral.

In addition to the insufficient CO_2 capture rates of CCS systems, the CO_2 storage option using EOR is an additional critical factor. Compared to geologic storage, such as in the Quest or Tomakomai project, which have not recorded leakage to date [36,41,42], studies specifically indicate that sequestration through EOR processes partially release CO_2 into the atmosphere. In a comparative study of 23 EOR projects, Olea et al. found that retention rates of injected CO_2 ranged widely from an inadequate 28 % to a maximum of 96 %, depending on the geology of the reservoir and the oil recovery technique used [44]. Since methane is the second most important GHG, methane emissions resulting from gas production are another critical issue that needs to be considered. However, quantifying these emissions has been difficult so far and is still a matter of controversy. According to a recently published UN report relevant studies regarding methane emissions “have been initiated and are underway” [45].

Furthermore, the CCS systems are technologically mature [32], but not widely used, as costs are too high. Collodi et al., comparing various CO_2 capture mechanisms, found that partial capture rate options (53–64 %) will increase the LCOH by 18–28 %, whereas an 90 % capture rate system will rise the hydrogen costs 1.45 times, compared to an SMR plant without CCS [31]. The cost structure associated with a 90 % flue gas separation, can be assumed to be the reason, why today’s systems rely on a partial capture system only.

In addition, the SMR-CCS technology has so far been financed mainly by government subsidies [40]: So, the Quest and Port Arthur plants have been realized with the help of government funding [32], whereas the Tomakomai project was financed by 36 companies [40]. The Quest, as well as the Port Arthur facility, also takes advantage of CO_2 tax credits [32]. In another study regarding real-world experiences of CCS project developers, Kapetaki et al. conclude that the commercial use of CCS plants is currently still limited due to economic and political factors. The dependence of the technology on government subsidies is also confirmed in this study, as well as on necessary revenue sources, such as CO_2 taxes or EOR [46].

Based on this section, it can be summarized that the few CCS plants are well tested and, in terms of technology maturity, the Quest and Port Arthur plants are the first two large-scale demonstration plants to be successfully operated in a relevant industrial environment [40]. Nevertheless, far more projects are needed to achieve the ambitious hydrogen targets. Even though CCS technology is easily scalable in that, according to Santos et al., existing SMR plants can be expanded with CCS units at little effort – in contrast to the construction of new power plants – the high investment costs significantly slow down area-wide CCS retrofitting. To make blue hydrogen compatible in terms of the energy transition, this technology must be further developed, with regard to cost reduction and increasing the overall capture rates and CO_2 retention rates. Due to residual CO_2 emissions persisting despite all efforts, blue hydrogen should only be applied as a bridging solution. However, since SMR currently produces the largest quantities of hydrogen and these plants can be retrofitted with CCS in a practicable manner, there is a large CO_2 savings potential in SMR-CCS in terms of the quantities of hydrogen produced – even if not 100 % of the emissions can be captured by this technology.

2.3. Methane pyrolysis

As at present, low-carbon hydrogen can currently only be produced to a limited extent with RE powered electrolysis or via SMR-CCS, alternative technologies must be considered. Therefore, the third hydrogen production technology to be discussed in this paper is methane pyrolysis.

Natural gas pyrolysis was first used around 1930 in the thermal black process and it therefore is a process that has been known for decades. These initial methane pyrolysis plants were operated to obtain high-quality carbon black (CB) as a reinforcing filler for the tire industry. The hydrogen obtained was fed to the firing process together with the other gaseous side products and thus also contributed to the heat required for the pyrolysis reaction. The thermal black process has been technically implemented in several variants, but currently with a CB yield of approx. 40 % it is only used sporadically for 4 % of the global CB market as the furnace black process turned out to be more economical and less polluting due to the higher yield of up to 70 % and the lower energy consumption required [47]. In the course of the energy transition, the focus in methane decomposition is no longer on the production of CB, but on the second reaction product – the hydrogen.

Under pyrolytic conditions, methane is split into its components solid carbon and gaseous hydrogen according to

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta_R H^{\circ} = 74.91\ kJ\ mol^{-1} \tag{3}$$

The required heat for this endothermic reaction can be provided by electricity or by burning of natural gas or hydrogen. In the course of climate change, natural gas should purely be used as a feedstock, whereas all energy required for the decomposition process should come from electricity, preferably from RE. A significant advantage of this reaction is that no oxidizing reactants, such as water vapor in the SMR process, can react with the methane, thus preventing the formation of CO and CO_2. Therefore, methane pyrolysis is considered a low-carbon hydrogen production technology and the product gas processing is less complex compared to that of SMR.

Methane pyrolysis can be divided into three technological implementations that mainly differ in the type of decomposition: thermal, via plasma, or catalytic. The pros and cons of these types of methane pyrolysis are briefly explained in the remainder of this section and summarized in Fig. 2.

Thermal decomposition needs temperatures higher than 1,000 °C, to ensure a significant methane conversion. If the required heat input occurs via the reactor walls, there is a risk that the carbon product will be deposited on the walls [48]. Moreover, thermal pyrolysis is often affected by reactor clogging [49]. This clogging behavior and the carbon deposits on the reactor walls result in an inadequate heat transfer. Therefore, this type needs further development in order to guarantee a continuous reactor operation without breakdowns [6,11].

Regarding a commercial and successfully operating pyrolysis plant, the most mature pyrolysis technology is the **plasma** process with temperatures over 2,000 °C. In the plasma reactor, methane is split by the high temperatures of the plasma torch. As a sufficiently large voltage is applied for producing the plasma, this methane pyrolysis technology has a very high electricity demand (11.1–21.1 $MWh_{el}\ t_{H2}$) [12,50]. But an advantage, that also applies to PEMEL, is the quick-start capability of plasma pyrolysis processes, making them compatible with fluctuating electricity of RE [11,49,51]. Further advantages are that the high temperatures can be limited locally to the plasma torch and that the process does not necessarily depend on any catalyst [9,51]. This results in a lower system complexity and a high purity of the carbon product, as it has not to be separated from any catalyst. Furthermore, compared to the thermal systems, carbon deposits occur here mainly on the plasma electrodes, that have to be replaced over time. In addition, instead of methane, also higher hydrocarbons can be cracked by the plasma variant [11,51].

In contrast, the **catalytic** decomposition requires rather low pyrolysis temperatures ranging from 500 to 1000 °C. The metallic catalysts used are mainly nickel or iron, with Ni-based catalysts exhibiting higher methane pyrolysis activity [52,53]. Advantages of molten metal catalysts are that the produced carbon floats to the catalyst's surface, where it can be removed more easily, and the heat transfer is more homogenous [11,51,54]. In the case of molten metals, however, higher temperatures of 900–1,200 °C are required, which are then close to those of non-catalytic thermal decomposition or this pyrolysis process is considered to be thermally controlled [53,55]. The most critical aspect is the deactivation of the catalysts by carbon deposits, resulting in a complex catalyst regeneration [11]. This problem was, e. g., successfully circumvented by Hazer. Due to the lower heat input and the affordable catalyst material, iron ore, the Hazer process becomes very cost-efficient, compared to the other two pyrolysis technologies [56]. In contrast, carbon catalysts with a typical pyrolysis temperature of 850–950 °C have the advantage that the carbon product obtained does not have to be separated from the catalyst afterwards [53].

Methane pyrolysis concepts, which have been researched, developed and partly put into operation, are listed in Table 4, covering technologies from TRL 3 onwards. As methane pyrolysis is the youngest among the technologies for hydrogen production compared in this paper, we give a short summary here on five implementations, due to their underlying promising concepts and higher TRL among the pyrolysis concepts.

A research association, including i. a. **BASF**, ThyssenKrupp and Linde, has developed a thermal pyrolysis reactor using the counterflow principle: In a moving bed reactor, carbon granules are fed against the natural gas stream flowing in from the lower part of the reactor. This incoming natural gas is pre-heated by the sinking hot carbon granules and the produced pyrolysis carbon accumulates on the granules. In the electrically heated reaction zone methane is heated to the reaction temperature of 1,200–1,400 °C and pyrolyzed. The hydrogen product

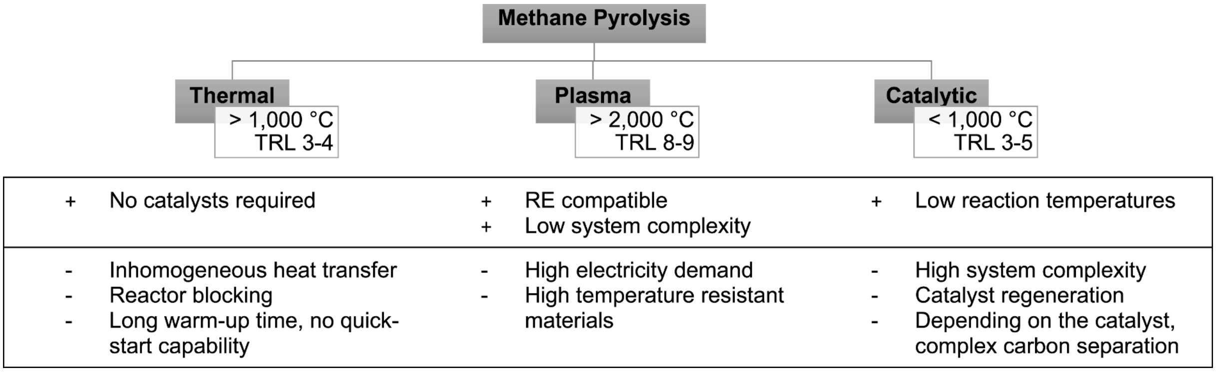

Fig. 2. Comparison of the advantages and disadvantages of the thermal, plasma and catalytic methane pyrolysis.

Table 4
Overview of methane pyrolysis processes.

Developer, Process	Principle (temperature)	Reactor concept	Target product	State of development	TRL
BASF [6,57,58]	Thermal (1,200–1,400 °C)	Moving carbon bed	H_2	Laboratory plant, R&D project for pilot scale (since 2012)	4
C-Zero [54,56,59–62]	Thermal (500–1,500 °C)	Packed bed with molten-Ni-based catalyst	H_2	Pilot plant will be constructed by the end of 2022 (since 2019)	4
KIT/IASS [10,63]	Thermal (up to 1,200 °C)	Liquid tin bubble column	H_2	Laboratory, R&D project for process development (since 2013)	3
SolHyCarb [64,65]	Thermal (up to 2,030 °C)	Concentrated solar power	H_2 & CB	Laboratory, R&D project, development was stopped (2006–2010)	3
Kværner: Karbomont plant [9,10,66]	Plasma (1,200–2,000 °C)	Plasma torch	CB	Seaport pilot plant (1992–2003) with subsequent production plant (1997–2003); Both dismantled	8
Monolith: Olive Creek Plant [67–70]	Plasma (2,200–2,400 °C)	Plasma torch	H_2 & CB	Pilot plant (2013–2018; dismantled) & production plant (since 2016; commissioning in 2020)	9
Atlantic Hydrogen [71–73]	Plasma (1,500–2,500 °C)	Plasma torch	H_2– enriched NG	Pilot plant (not put into operation), development was stopped due to bankruptcy (2005–2015)	5
Tomsk Universities [74,75]	Plasma-Catalytic (400–1,000 °C)	Microwave, Ni catalyst bed + plasma torch	H_2	Laboratory, no further information on scale-up (since 2008)	3
Hazer Group [76,77]	Catalytic (600–1,000 °C)	Fluidized bed with iron ore catalyst	H_2 & Graphite	Pilot plant, commercial demonstration plant will be constructed in 2022 (since 2010)	5
UOP: Hypro process [10,78]	Catalytic (800–1,100 °C)	Fluidized bed with Ni catalyst	H_2	Laboratory plant, development was stopped (1963–1966)	4
Florida Solar Energy Center [79,80]	Catalytic (850–1,000 °C)	Fluidized bed with C catalyst	H_2	Laboratory, no information on further development (2003–2005)	3

leaving the reactor is cooled by pre-heating the carbon granules entering the reactor from the top. The carbon particles agglomerate and grow as they pass through the reactor. The hydrogen stream is then subjected to downstream purification stages to remove undesirable residual carbon particles and dust [6,57,58]. The solid carbon particles leaving the reactor are conditioned and the fraction with inadequate particle size is recycled back into the reactor. The coarse material is separated off as the carbon product.

Parallel to a direct electrical heating of the reaction zone by resistance heating, the heat-input was tested by means of induction [6,57]. However, since reactor blockages (reactor wall and/or moving bed) were observed for both heating concepts, a new reactor design has to be developed in further R&D steps according to BASF [57].

The laboratory plant was run on pure methane, but further tests by using natural gas have shown that the higher hydrocarbons contained in the feed gas had no significant impact on the methane conversion [6]. According to BASF, there is still further R&D necessary for scaling-up their technology from laboratory to pilot scale, which is planned in ongoing research projects [57]. A hydrogen capacity of 10,000 $Nm^3\ h^{-1}$ was specified for the future pilot plant which will be followed by the first commercial unit planned for 2025 [6,57].

C-Zero LLC uses a molten-Ni-based catalyst in a multi-phase pyrolysis bed reactor [59]. According to the patent application, C-Zero initially researched a pyrolysis process based on molten salts [59]. However, in February 2021, the company announced that they decided to use Ni-based catalysts [60].

The heat input into the bubble column reactor is transferred via electric heating elements, that are immersed in the molten material. Before the feed gas enters the main pyrolysis reactor, it is pre-heated in two successive heat exchangers by extracting heat from the hot product gas stream: The feed gas is heated in the first heat exchanger to max. 850 °C and enters a first pyrolysis reactor containing carbon or nickel catalysts to pyrolyze most of the higher C_{2+} hydrocarbon components of the feed gas. This pyrolyzed feed stream is then heated to 700–1,100 °C in the second heat exchanger before it enters the main pyrolysis reactor. The pre-heated methane is introduced into the main pyrolysis reactor via a gas distributor, disposed at the bottom of the reactor, forming bubbles in the liquid reaction medium. When the methane comes into contact with the hot catalyst material, the decomposition process takes place at temperatures of up to 1,500 °C [54,59]. According to these high temperatures, this catalyst using methane pyrolysis process is considered thermally controlled.

Due to density differences, the solid aggregated and grown carbon particles accumulate and float on the surface of the molten material. According to the patents, these carbon particles are extracted from the molten material and discharged from the reactor by various methods, e.g. an auger or a cyclone. Since the high temperatures in the reactor can result in vaporized catalyst material leaving the reactor with the product gas, this gas mixture is cooled in a downstream heat exchanger condensing the catalyst and recycling it back into the process [54,59].

C-Zero focuses exclusively on the hydrogen produced and does not intend to produce an additional high-quality CB product. With the aim of achieving the lowest possible LCOH, this solid carbon by-product is to be sequestered, thereby saving the money and energy that would be required for the processing of a commercial, high-quality carbon product. According to C-Zero, these savings should reduce costs to such an extent that their process provides hydrogen at lower costs than a SMR-CCS system [60,61].

With funding from the U.S. Department of Energy, C-Zero's reactor design was developed and improved in 2020. C-Zero is currently working on transferring its technology from laboratory testing to pilot-scale and will have its first commercial pilot plant completed by the end of 2022, which will be able to produce 250 kg of hydrogen per day [60]. C–Zero plans to use biogas in the future to make its process even CO_2-negative [61]. Furthermore, emissions are reduced as C-Zero's "drop-in decarbonization system" can be built next to a borehole or on-site at a hydrogen consumer, reducing natural gas or hydrogen supply chain emissions, respectively [61,81].

The best-known methane pyrolysis process based on a plasma is the **Kværner** process. As early as 1992, the Norwegian company was using a plasma, generated by graphite electrodes, to produce CB in its 3 MW pilot plant [66]. Five years later the industrial "Karbomont Plant" with a carbon yield of 20,000 $t\ yr^{-1}$ and a hydrogen production of 70 Million $Nm^3\ yr^{-1}$ went into operation [9]. The main product of the Kværner process was CB, whereas the obtained hydrogen was recirculated to the reactor as plasma gas. A critical aspect of this process was the pyrolysis-induced accumulation of carbon deposits blocking the electrodes, resulting in a large electrode consumption. Due to insufficient quality of the CB, both plants have been decommissioned in 2003 [6,9].

Nowadays, one of the most outstanding methane decomposition plants is **Monolith's** "Olive Creek Plant". Ten years after the decommissioning of the Kværner plants, the company Monolith Materials – today Monolith Inc. – together with the research group of Fulcheri et al. adopted this process in a slightly modified form and developed it further

[6,9]. Monolith has seen the potential in the Kværner reactor principle and operates with its “Olive Creek Plant” in Nebraska the most advanced methane pyrolysis plant to date.

In this pyrolysis development natural gas is super-heated and decomposed in a plasma reactor using graphite electrodes powered by RE. The feedstock used in the Monolith plant is preferably methane, whereby the process allows higher hydrocarbons and even heavy fuel oil. A plasma-arc is created and an 2,200–2,400 °C hot plasma stream enters the reaction zone decomposing the methane. After the reactor the carbon-hydrogen gas stream with a temperature of approx. 1,500 °C is cooled to <250 °C using heat exchangers which pre-heat the methane feed at the same time. Using a filter, the carbon is separated from the hydrogen. A part of this approx. 95 % pure hydrogen tail gas is recycled to the reactor. One part of the recycled hydrogen is electrically heated and used, like in the Kværner process, as the plasma gas. The other recycled hydrogen gas is fed into the reactor, to cool and control the temperature of the CB forming reaction as well as the product’s quality [9,69,70].

In the patent it is described that in previous processes, such as that of Kværner, the quality of the plasma carbon was inadequate in terms of rubber performance compared to furnace black, and that Monolith has solved this problem in its process. The carbon nanoparticles produced herein can reinforce elastomer compounds, making them more useful in applications such as tires or rubber hoses. In addition, it is pointed out that the Monolith process has significantly lower emissions (0,3 $kg_{CO2}\ kg_C^{-1}$) than the furnace process, which emits not only a huge amount of CO_2 (2,3 $kg_{CO2}\ kg_C^{-1}$) but also nitrogen and sulfur oxides [67,82]. Moreover, the carbon yield with more than 90 % is higher compared to the 70 % of the furnace process [47,69]. A recent press release details the company’s collaboration with the Goodyear Tire & Rubber Company to use the sustainable carbon as a filler enhancer [82]. While the technology was initially designed exclusively for the production of CB, Monolith now also promotes its carbon-free hydrogen [67,68]. Thus, the Olive Creek Plant is the first commercial pyrolysis facility, marketing both hydrogen and CB. The use of 100 % RE via a power purchase agreement for generating the necessary electric arc limits the CO_2 emissions to the ones of the natural gas supply chains [83].

The “Seaport” pilot plant, which had been operating successfully for three years, was dismantled in 2018 without giving any reasons. With initial results from this pilot plant the “Olive Creek Plant” was built in 2016 and has been in operation as a commercial plant, however, since its commissioning in Q2 2020 [67,68]. Since then, the plant has been supplying its customers with 14,000 $t_C\ yr^{-1}$ [84]. Monolith is currently working on expanding the “Olive Creek Plant” and the expansion planned for 2025 will increase the plant’s current capacity by a factor of 13 to 194,000 $t_C\ yr^{-1}$. Using the hydrogen produced in these two plants (nearly 50,000 $t_{H2}\ yr^{-1}$) and nitrogen extracted from the air, 275,000 tons of green ammonia will be produced annually [68,85].

A process that uses catalysts to lower the pyrolysis temperature is currently being developed by the Australian company **Hazer** Group with the target products hydrogen and graphite. In this project, supported by the Australian government, a cheap catalyst material [60], raw iron ore, is used in a 3-stage fluidized bed reactor [10,76,77]. At reactor temperatures of approx. 600–1,000 °C, natural gas is fed into the reactors in series, from the high-pressure to the medium-pressure to the low-pressure reactor. In each reactor a portion of the gas interacts with the surface of the catalyst particles and forms hydrogen and graphite. By carbon accumulation on the catalysts’ surface, metal carbide nanofragments are released from the catalyst material by an increasing intergranular pressure, so that further catalytic material is exposed. As a result of this reaction process a catalyst recovery is not necessary, making the Hazer process more profitable. Due to the low density of these small graphite particles, they can be easily discharged from the reactor together with the hydrogen-methane gas mixture. By using a subsequent nano-particle filter, the carbon product can be separated from the gas flow. This principle of reactors connected in series and the counter-current arrangement of the gas and catalyst streams ensures a high conversion rate of the feed gas and a high graphitic carbon quality as well as the possibility to control these parameters by changing the pressure and temperatures in the reactors [76,77]. For producing pure hydrogen, the gas mixture is then cleaned of unreacted methane and other by-products, which are recycled to the reactor, in a PSA [76,77]. The produced carbon emerges from the process as 80–95 % pure, high-quality, and highly crystalline graphite, which is postulated to be very similar to the graphite used in lithium-ion batteries [56].

The basic Hazer process was developed at the University of Western Australia. The Hazer Group currently operates a pilot facility with a methane conversion of 92 % [76] and has begun construction of a commercial demonstration plant. This upcoming plant will use biogas from wastewater treatment plants as feedstock, which will be pretreated removing the CO_2 contained, and is planned to produce 100 tons of hydrogen per year [62].

3. Comparison of low-carbon hydrogen production technologies

In this section the three types of low-carbon hydrogen production technologies are compared with respect to their TRL, scalability, economic and ecological aspects as well as the influence of by-products on their efficiency.

3.1. Technology readiness

The TRL of methane pyrolysis, covers R&D up to commercial operating systems. Table 4 shows (i) that plasma pyrolysis has already been implemented on an industrial scale and is considered feasible (Monolith, TRL 9, and Kværner, TRL 8), (ii) that catalytic pyrolysis is catching up through the Hazer pilot plant (TRL 5) and (iii) that a rapidly growing C-Zero company (planned commissioning of a pilot plant in 2022, TRL 4) and BASF (TRL 4) continue research on thermal pyrolysis to scale–up their plants. Other researched concepts have been stopped at an early stage (TRL 3–5) due to several reasons like insufficient methane conversion, problems with reactor blocking as well as catalyst deactivation by the produced carbon or bankruptcy [6,9,56,63,70,73].

Although some methane pyrolysis and SMR-CCS plants show a mature TRL, it must be noted that this is only a matter of a few systems, compared to several commercially operated AEL systems, some of which have been installed for decades. Based on operational experience, SMR-CCS is the youngest technology (commissioning years: 2013–2016) with eight years of operation of the Port Arthur plant so far [32,40]. Plasma pyrolysis has 8–13 years of operation with the Kværner plants until both were dismantled due to the insufficient CB quality [9]. In addition, the enhanced Kværner process was operated by Monolith in its pilot plant for over three years until it entered commercial operation in 2020 [68]. In contrast, AEL was already able to record almost 50 successful years of operation with the initial large-scale plants in Norway or Egypt [16]. Thus, AEL remains the most proven low-carbon technology in terms of technological maturity and years of operating experience.

Overall, further R&D is needed for all three technologies to further mature the partially proven economic concepts and to be able to move the promising systems that are currently still in prototype status to a higher TRL.

3.2. Scalability

Hydrogen-production targets require in the coming decades not only to successfully increase the TRL, but also to rapidly introduce proven technologies to the market. Therefore, the question is answered to what extent it is possible to scale up the three low-carbon hydrogen technologies and, above all, in a timely manner.

Electrolysis is characterized by modularization. Several electrolysis stacks can be connected with little effort, leading to a scalability of the output into the MW-range [13]. The Aswan Dam AEL has demonstrated that large-scale hydrogen production up to 156 MW is possible. However, the largest plant currently in operation (AEL) has a hydrogen production-capacity of 25 MW (3,700 t_{H2} yr^{-1}) [16]. To illustrate the rapid scaling of water electrolysis in recent decades, the IEA summarizes its performance: While electrolysis capacities were still in the kW range in the initial 2010s, a high number of 1.5 MW plants were realized in the 2017–2019 period, with the largest electrolyzer reaching 6 MW [21]. This maximum capacity for 2019 was more than tripled by Air Liquide's 20 MW PEMEL in 2021 [23]. If the announced 100 MW PEMEL projects by Hydro-Québec and Shell Inc. are realized [86,87], the current PEMEL capacity can be increased by another five times in a few years. This data highlights the rapid scaling potential of electrolysis and especially of the RE-compatible PEMEL over the last few years.

Although only a few SMR plants are currently equipped with a CCS unit, according to Brändle et al., CCS units can be added simply to existing SMR plants [88]. Thus, the SMR-CCS technology is considered easily scalable. According to an analysis by IRENA, the previously set scale-up targets for CCS have not been met due to various factors, such as the abandonment of projects, the costs or the lack of public acceptance, and the retrofitting of existing plants with CCS has been slower than expected [2]. Therefore, R&D needs to rise, bringing more CCS systems, including the CO_2 capture from the flue gas, to a mature level, to benefit from their scalability [32]. As SMR is currently the most widely used hydrogen production process [14], retrofitting these existing hydrogen plants would be easier compared to the construction of a completely new hydrogen facility and can achieve rapid positive results at low effort ("low hanging fruits"), making the SMR-CCS technology more quickly scalable.

According to C-Zero, methane pyrolysis plants are scalable to the extent that they will be competitive with SMR facilities in terms of the amount of hydrogen produced (100,000 t_{H2} yr^{-1}) [81]. For comparison, one of the Port Arthur SMR-CCS plants has a hydrogen capacity of 90,000 t_{H2} yr^{-1} and the largest pyrolysis plant to date, which had been operated by Kværner, had produced approx. 6,300 t_{H2} yr^{-1}. The production capacity of Monolith's plant is about 30 % less than that of Kværner [9,37,68]. The largest AEL currently produces 3,700 t_{H2} yr^{-1}, followed by the most powerful PEMEL with about 3,000 t_{H2} yr^{-1} and an HTEL system with just under 530 t_{H2} yr^{-1} [18,23,24]. With such annual production capacities, existing electrolyzers are inferior to the natural gas-based technologies discussed herein. In addition, the expansion of the "Olive Creek Plant" in the near future (2025) will result in a pyrolysis hydrogen capacity of almost 50,000 t_{H2} yr^{-1} [68], whereas, e. g., the world's largest PEMEL, planned in Canada for 2023, will only achieve about one fifth of this amount [86].

With a good quick-start capability plasma pyrolysis has an advantage over the other pyrolysis technologies, can therefore compete with PEMEL and can potentially be scaled faster through targeted incentives [11,12].

Summing up, electrolysis is more easily scalable due to module expansion, but has not yet reached the capacities of initial methane pyrolysis plants. Compared to methane pyrolysis, SMR-CCS is more scalable due to the simpler extension of a CCS system to the abundant existing SMR plants and their high achievable capacities.

3.3. Economic comparison

Several techno-economic analyses for each of the three low-carbon hydrogen production technologies, discussed herein, can be found in the literature. The price ranges can be summarized as follows – however, it must be mentioned that a wide spread of cost ranges for electricity, water and natural gas was found in the references used for the LCOH (s. footnote of Table 5):

The electrolysis LCOH have a big bandwidth from 2.8-8.7 € kg_{H2}^{-1}, whereby costs for AEL range typically between 2.8-5.5 € kg_{H2}^{-1}, for PEMEL between 2.5-7.7 € kg_{H2}^{-1} and HTEL can increase LCOH towards the upper bandwidth price. It should be noted that this range includes both electricity from RE and from an electricity mix [4,12,89]. Thus, Timmerberg et al. have calculated the cost of renewable AEL to 3.5 € kg_{H2}^{-1} (2.7–8.7 € kg_{H2}^{-1}), whereas using electricity from combined cycle power plants reduces the LCOH to 2.6 € kg_{H2}^{-1} (2.0–6.0 € kg_{H2}^{-1}) [12]. Since only RE should be used for electrolysis, as otherwise the emissions of this technology would rocket due to the large amounts of fossil-based electricity required, the higher LCOH are taken into account.

While SMR is considered the most cost-effective hydrogen production method, CO_2 capture and storage pose challenges to both the efficiency and economics of SMR plants. Therefore, the LCOH for SMR (0.6–1.3 € kg_{H2}^{-1}) increases up to 1.1–2.2 € kg_{H2}^{-1} by implementing a CCS system [4,31].

The LCOH for pyrolysis range from 1.4 to 6.2 € kg_{H2}^{-1}, whereby the LCOH for a small-scale plasma system with up to 6.2 € kg_{H2}^{-1} are at the upper limit and 1.4 € kg_{H2}^{-1} can be achieved by molten metal reactors [11,12,14].

Machhammer et al. compared low-carbon hydrogen production technologies on a financial and ecological basis, using the price of an electricity mix. It was found that LCOH by methane pyrolysis (3.2 € kg_{H2}^{-1}) is about 50 % of the electrolysis route (approx. 7.9 € kg_{H2}^{-1}) [7]. As expected, the main cost driver in water electrolysis is the demand for electricity, whereas the natural gas price dominates the SMR costs (2 € kg_{H2}^{-1}) [7]. The costs for pyrolysis are highly dependent on the price of the natural gas required and to lesser extend to the price of electricity, with a much higher electricity consumption for plasma systems, of course [7]. Easy access to inexpensive natural gas is to be preferred for methane pyrolysis and countries with high natural gas reserves, such as Russia or Saudi Arabia, offer great potential for cost competitive methane decomposition systems.

In conclusion, the lowest LCOH can be achieved by SMR with CCS, followed by the intermediate LCOH of methane pyrolysis and finally the highest LCOH by electrolysis.

3.4. Influence of by-products

The use of profitable by-products can increase the efficiency as well as the cost-effectiveness of the three hydrogen production technologies.

As addressed in Section 2.2, the SMR-CCS process can generate profits from the captured CO_2. For example, the Port Arthur facility in Texas prefers the EOR process to geological storage because of the economic profit [32,37]. However, in the course of decarbonization, the EOR method must be critically evaluated due to insufficient CO_2 retention rates. Therefore, a more promising process for the future, which should be preferred over CCS, is CCU, e. g., to convert the captured CO_2 into synthetic fuels or to use it in the food industry.

As mentioned before, methane pyrolysis is accompanied by solid carbon. Based on the ratio of the molar mass of the products carbon and hydrogen of 3:1, it becomes clear why the former natural gas pyrolysis processes focused on the CB production. Comparing the sequestration of CO_2 from the SMR process and of the pyrolysis carbon, solid carbon has a clear advantage over the volatile CO_2. However, due to the economics, focus needs to be put on the commercialization of the carbon by-product. With regard to GHG emissions, the pyrolysis-carbon should not be burned, but either stored or used, e. g. as Monolith does, for the tire industry.

The carbon produced has high purity, is considered a rare raw material and can be used in a wide variety of applications, such as a reinforcement agent in the rubber industry or as a pigment for printer's ink. Moreover, it can be processed in asphalt or further developed into high-quality carbon fibres [11]. Prices range from 0.4 to 2.0 € kg_C^{-1} for CB, to more than 9 € kg_C^{-1} for graphite and up to 100 € kg_C^{-1} for carbon fibers [7,11,90]. Since the carbon is a by-product anyway and is produced in an almost climate-neutral manner, it can be assumed that this "green" alternative would drive conventional carbon production technologies out of the market.

As selling the by-products of methane pyrolysis and electrolysis decreases the LCOH, the following product sale prices are assumed in the study of Machhammer et al.: A sales price of 0.2 € kg_C^{-1} for carbon with a moderate purity and 0.05 € kg_{O2}^{-1} for the oxygen product, resulting in a decreased LCOH of 2.6 € kg_{H2}^{-1} (decrease of approx. 18 %) for pyrolysis hydrogen and 7.5 € kg_{H2}^{-1} for electrolysis hydrogen (decrease of approx. 5 %) [7]. In the case of the high-purity graphite product from the Hazer process, which could be used in lithium-ion batteries, the sales-price for the carbon by-product could increase by up to 45 times compared to the one used in the study of Machhammer et al. for a CB product. Timmerberg et al. found in their sensitivity analysis that LCOH of relatively low 2.0 € kg_{H2}^{-1} can be reduced to zero if the carbon product can be sold for approx. 0.75 € kg_C^{-1} [12].

It has to be mentioned that among these carbon products, carbon black occupies the largest market size with an annual global demand of 16.4 Mt_C yr^{-1} [11]. Assuming that the current global hydrogen demand of 90 Mt_{H2} yr^{-1} is met exclusively by turquoise hydrogen [13], would result in a carbon by-product yield of 270 Mt_C yr^{-1}, corresponding to 94 % of pyrolysis carbon that cannot be sold. Therefore, the profit of selling the carbon by-product is severely limited due to the small global market and, once methane pyrolysis has been ramped up, it will contribute only marginally to the reduction of the methane pyrolysis LCOH. In the future, global demand for graphite (0.25 Mt_C yr^{-1}) and needle coke (1.54 Mt_C yr^{-1}) is expected to grow due to the increasing demand for lithium-ion batteries [11]. However, these amounts have to increase immensely to make a difference in the before stated estimation.

Concluding, the sale of the carbon product is an economically important factor and should be considered, especially for the first methane pyrolysis plants to be commissioned. Electrolysis oxygen also increases the economics of the process, but to lesser extent than for methane decomposition, with the global oxygen market being more promising compared to the smaller global carbon market so far.

3.5. *Ecological comparison*

According to the IEA, the global – currently predominantly grey – hydrogen production (90 Mt_{H2} yr^{-1}) is responsible for 635 Mt_{CO2} yr^{-1}, which is accountable for approx. 2 % of the world's annual anthropogenic CO_2 emissions [13,14]. Thus, the CO_2 emissions of each low-carbon hydrogen technology are summarized in this section.

CO_2 emissions for SMR decrease from about 9–11 kg_{CO2} kg_{H2}^{-1} to a range between 1 and 4 kg_{CO2} kg_{H2}^{-1} by retrofitting SMR with a CCS system [7,14,31]. This wide bandwidth results from the various CCS systems with different CO_2 capture rates. Taking the actual capture rates of 37 and 54 % (s. Table 3) into account and relating them to the usual SMR emissions of 11 kg_{CO2} kg_{H2}^{-1}, the emissions of blue hydrogen result in about 5.1–6.9 kg_{CO2} kg_{H2}^{-1}. In addition, the calculations of a recently published study have shown that the life cycle CO_2 emissions of blue hydrogen are only 9–12 % lower than those of gray hydrogen, taking into account both CO_2 emissions and emissions of unburned fugitive methane [91]. For this reason, and the fact that 100 % of the emissions can never be captured, CCS should be seen critically and, if so, remain only a bridging technology.

Since methane pyrolysis is predominantly in a rather low TRL, the results of the few studies differ with their varying assumptions: Due to Dagle et al., catalyst regeneration by burning of the carbon results in high CO_2 emissions that are nearly comparable to those of SMR [11]. Therefore, this variant of catalyst regeneration should not be applied and will not be considered in the further course of this work. Moreover, the pyrolysis CO_2 emissions can only be maintained at this level if the produced carbon is not burned in any subsequent process.

Parkinson et al. compare four different heating concepts for a molten metal reactor, estimating the following CO_2 emissions (excluding natural gas supply chain emissions): An electric arc furnace concept (3.1 kg_{CO2} kg_{H2}^{-1}), an electric arc furnace concept adding catalysts to the molten metal (2.7 kg_{CO2} kg_{H2}^{-1}), natural gas fired heating system (1.5 kg_{CO2} kg_{H2}^{-1}) and a hydrogen fired system (0 kg_{CO2} kg_{H2}^{-1}) [8]. As in the Hazer process iron oxide catalyst particles are reduced to iron by methane, small amounts of CO_2, CO, and water are produced. For this reason, the Hazer Group assumes a rough emission reduction of at least 50 % for its process compared to a conventional SMR plant, corresponding to 4.5–5.5 kg_{CO2} kg_{H2}^{-1} [56,77]. Monolith states for its current operating plasma plant, using exclusively renewable electricity, very low CO_2 emissions of 0.45 kg_{CO2} kg_{H2}^{-1} [68]. In a previous techno-economic study regarding the BASF-concept, thermal pyrolysis based on a moving carbon bed was considered: Under the assumption of an electricity mix (0.35 t_{CO2} MWh_{el}^{-1}) the CO_2 emissions result in 4.37 kg_{CO2} kg_{H2}^{-1} split into emissions of the electricity required (2.53 kg_{CO2} kg_{H2}^{-1}) and natural gas supply chain emissions (1.84 kg_{CO2} kg_{H2}^{-1}) [7].

Moreover, the electricity source has a significant impact on the emissions of the processes. In the case that electrolysis is not compatible with fluctuating electricity from RE, this leads to significantly higher GHG emissions compared to the other two technologies. Thus, in the study by Machhammer et al., electrolysis with an electricity mix results in CO_2 emissions of 21.38 kg_{CO2} kg_{H2}^{-1} [7]. Other studies report GHG emissions of 30 kg_{CO2} kg_{H2}^{-1} [12] to 40.50 kg_{CO2} kg_{H2}^{-1} [92], so that these CO_2 emissions exceed those of the turquoise hydrogen production (Machhammer et al.: 4.37 kg_{CO2} kg_{H2}^{-1} [7]) by more than 9 times. Summing up and for a better comparison based on equal assumptions, Fig. 3 summarizes the CO_2 emissions in relation to the energy source used – electricity or natural gas. Herein, the following carbon footprints have been applied: 0.35 t_{CO2} MWh_{el}^{-1} for an electricity mix and 0.46 t_{CO2} t_{CH4}^{-1} for the natural gas supply chain [7]. The emissions of SMR are divided into the process emissions of 9.24 kg_{CO2} kg_{H2}^{-1} and the supply chain emissions of 1.55 kg_{CO2} kg_{H2}^{-1}. The SMR-CCS emissions are the average of the emissions emitted by the currently operating plants (6 kg_{CO2} kg_{H2}^{-1}) plus the natural gas supply chain emissions (1.84 kg_{CO2} kg_{H2}^{-1}) including the assumption of an increased natural gas amount of 20 % for the latter, due to the capture systems. For methane pyrolysis the data from Machhammer et al. has been applied [7], as it is in the range with the other given CO_2 emissions listed above.

In addition to the CO_2 emissions, scaling-up electrolysis and SMR with CCS, both of which require water for their reactions, will increase the water consumption in the hydrogen economy extensively. Stoichiometrically, electrolysis requires 8.9 kg_{H2O} kg_{H2}^{-1} and SMR without CCS requires about 4.5 kg_{H2O} kg_{H2}^{-1}. Thus, if the hydrogen that has so far been produced predominantly by SMR is completely replaced by green hydrogen, the water demand would double. According to losses, the water consumption of the electrolysis can increase and due to the moderate efficiencies and the connection of a CCUS unit, the IEA specifies 13–18 kg_{H2O} kg_{H2}^{-1} for an SMR-CCUS plant [13]. It should be highlighted that water is not required for the methane pyrolysis reaction itself and, therefore, turquoise hydrogen is an attractive and water-saving hydrogen production technology.

4. Results and discussion

The entire results of this work are summarized in this section and the comprehensive comparison of the low-carbon hydrogen production processes addressed herein is discussed. In order to better compare the characteristics achieved so far, the most important data of the individual technologies are listed in Table 5.

With years of operational experience for various AEL plants, this electrolyzer technology is the most commercially mature hydrogen production technology discussed herein. Compared to AEL, some PEMEL systems, a large-scale operational plasma pyrolysis system and a few SMR-CCS systems have reached commercial maturity as well, but still need further development to increase the number of operating systems. Even more effort is needed for catalytic and thermal pyrolysis as well as for HTEL regarding their lower **TRL**.

In terms of **scalability**, electrolysis benefits from the ease of module

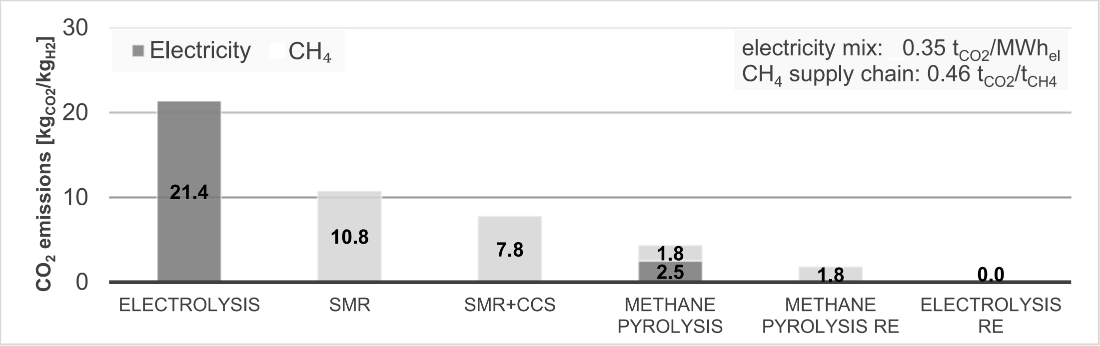

Fig. 3. Comparison of the CO$_2$ emissions [kg_{CO2} kg_{H2}^{-1}] of hydrogen production technologies – electrolysis and methane pyrolysis using either electricity from RE or from an electricity mix and SMR with or w/o CCS [7,14].

Table 5
Comparison of the technologies electrolysis, SMR-CCS and methane pyrolysis.

	Electrolysis		SMR-CCS	Pyrolysis	
TRL [–]	AEL:	8–9	8–9	Plasma:	8–9
	PEMEL:	7–8		Catalytic:	3–5
	HTEL:	6–7		Thermal:	3–4
Quick-start capability resp. RE compatibility	AEL:	no	n. a.	Plasma:	yes
	PEMEL:	yes		Catalytic:	no
	HTEL:	no		Thermal:	no
Max. H$_2$-capacity [t_{H2} yr^{-1}]	< 3,700		>100,000	< 4,500	
(Upcoming projects [t_{H2} yr^{-1}])	(11,100)		(n. a.)	(50,000)	
Enthalpy [kJ mol_{H2}^{-1}]	285.83		63.28	37.46	
CO$_2$-emissions [kg_{CO2} kg_{H2}^{-1}]	0		5.1–9.8	0–4.4	
LCOH [€ kg_{H2}^{-1}] [a)]	2.8–8.7		1.1–2.2	1.4–6.2	

[a)] A wide spread of cost ranges for electricity, water and natural gas was found in the references used for the LCOH: electricity 35-110€/MWh; water 0.2 €/m^3; natural gas 4.1–6 €/GJ.

expansion, but years of R&D have not yet been able to achieve the capacities of plasma pyrolysis, which recently entered commercial operation. In addition, the expansion of Monolith (50,000 t_{H2} yr^{-1}) planned for 2025 testifies to a significant scaling progress of methane pyrolysis compared to electrolysis with an upcoming project capacity of 11,100 tons per year. In this comparison, SMR-CCS is more scalable due to the simpler combination of a CCS system with the many SMR plants currently in operation, including their high hydrogen production capacities. However, in the case of blue hydrogen, the high CO$_2$ emissions must be taken into account, which at the current stage of development make this technology no alternative worth comparing with the CO$_2$-free green and almost climate-neutral turquoise hydrogen options.

In terms of the energy to be applied, methane pyrolysis requires the lowest **enthalpy** per hydrogen molecule produced. With 37.46 kJ mol^{-1} the pyrolysis reaction is energetically slightly favorable compared to SMR with 41.28 kJ mol^{-1}, especially if the enthalpy of vaporization is also included for SMR (63.28 kJ mol^{-1}). Compared to electrolysis (285.83 kJ mol^{-1}), the reaction enthalpy of methane pyrolysis is 7.7 times lower.

The IEA points out that meeting today's hydrogen demand exclusively by electrolysis, would result in an exorbitant electricity consumption of 3,600 TWh [14]. Depending on the process, methane pyrolysis requires 3 to 8.5 times less **electrical energy** than electrolysis: Assuming that the necessary heat supply for methane pyrolysis is provided by electrical energy, Ausfelder et al. determined an electricity demand of 9.5 MWh_{el} t_{H2}^{-1}. Splitting water, on the other hand, is reported with 51.6 MWh_{el} t_{H2}^{-1} and uses almost 5.5 times more electricity than the pyrolysis reaction [19]. In their comparative study, Machhammer et al. calculate a specific electrical energy demand of 61.1 MWh_{el} t_{H2}^{-1} for a pressurized electrolysis and 7.2 MWh_{el} t_{H2}^{-1} for a thermal pyrolysis with an electrical resistance heating [7], so that the electrolysis power demand is 8.5 times higher herein. Timmerberg et al. report an electricity consumption of 2.3–19.8 MWh_{el} t_{H2}^{-1} for thermal and catalytic pyrolysis, 11.1–17.8 MWh_{el} t_{H2}^{-1} for plasma systems and 51.3–53.6 MWh_{el} t_{H2}^{-1} for AEL. These values are meant to illustrate the fact that with the same amount of electricity, significantly more hydrogen can be obtained by splitting methane using pyrolysis than by splitting water using electrolysis. In terms of an efficient hydrogen production that uses RE electricity, methane pyrolysis is a viable alternative with a much lower electricity consumption.

Furthermore, plasma pyrolysis can be combined well with **RE** in addition to PEMEL due to its high dynamics. Although both systems just mentioned are **quick-start capable**, it must be kept in mind that plasma pyrolysis has a higher TRL compared to PEMEL. In addition, the current commercial plasma system achieves a higher hydrogen capacity of 6,000 Nm_{H2}^{3} h^{-1} than the currently largest operating PEMEL with only 3,800 Nm_{H2}^{3} h^{-1}.

CO$_2$ emissions of methane pyrolysis are ranging between zero and 4.4 kg_{CO2} kg_{H2}^{-1}. Under certain conditions – operated with RE and no burning of carbon for catalyst regeneration, etc. – the emissions may even be limited exclusively to natural gas extraction and transport. Although natural gas pyrolysis will always have some residual CO$_2$ emissions, due to emissions along the natural gas supply-chain, lower emissions as for SMR-CCS with its insufficient capture rates can already be achieved today if the electricity demand is covered by RE, as in Monolith's plant. Moreover, it must be made aware of that some pyrolysis concepts with the need of continuous heat supply are not comparable with the fluctuating electricity form RE and rely on the emissions of the electricity mix used. In this case, the CO$_2$ emissions result in the highest values of the range shown in Table 5. However, the same applies to electrolysis, as only PEMEL shows sufficiently high dynamics. Since the energy demand for electrolysis is very high, not using 100 % RE would lead to extraordinarily high emissions of 21–41 kg_{CO2} kg_{H2}^{-1} [7,12,89]. Summing up, in terms of CO$_2$ emissions methane pyrolysis ranges almost in the middle of the green (0 kg_{CO2} kg_{H2}^{-1}) and blue (5–10 kg_{CO2} kg_{H2}^{-1}) hydrogen production processes.

An argument in favor of methane pyrolysis is that this reaction itself does not require any **water** compared to the other two technologies and therefore offers a decisive and, above all, resource-saving advantage.

Because of the high annual low-carbon hydrogen production volume by SMR-CCS systems, the **LCOH** for these facilities is the lowest in this comparison. With an eye on the current natural gas price, it becomes increasingly important to install methane pyrolysis on site of large natural gas reserves with access to affordable natural gas costs or to limit at least natural gas transport costs. Thus, a higher natural gas price decreases the delta between the pyrolysis and electrolysis LCOH in favor of the latter technology if the electricity price stays stable.

The LCOH of methane decomposition processes are on average between those of SMR-CCS and electrolysis, and may approach those of

SMR-CCS depending on the carbon **by-product** produced. To date, an 18 % reduction in pyrolysis LCOH has been calculated from the sale of CB, but this can be further increased by higher quality carbon products. Compared to the sale of the oxygen product, which is calculated to reduce the electrolysis LCOH by only 5 %, future reductions from the sale of the by-product are not expected to be as large for this technology as for methane pyrolysis. However, it should be noted that due to the small world-market for CB, 100 % offtake of CB is an initial situation where only the first methane pyrolysis plants can benefit from.

In conclusion, water electrolysis is indisputably an important technology to be pursued in order to render the electricity increasingly generated from RE long-time storable in the form of hydrogen. This technology is indispensable for the decarbonization of the entire energy system. However, according to the current state of development with regard to the large quantities of hydrogen to be produced, this technology alone cannot achieve the defined goals in the short term. Therefore, further low-carbon technologies are needed. As has become apparent in the course of this work, however, this cannot be achieved solely by expanding the existing SMR plants with CCS systems, since these will continue to emit large quantities of CO_2 even if the current capture rates are improved in the future. In order to ensure a rapid hydrogen market ramp-up worldwide, blue hydrogen should be used partially and exclusively as a bridging technology. Whether methane pyrolysis with its currently few plants is the key to closing the gap between green and blue hydrogen remains to be seen. However, it can be concluded that this technology has a high potential as a low-carbon hydrogen production technology, as it requires less energy and comes at lower cost than water electrolysis on the one hand, and clearly emits lower amounts of CO_2 than SMR-CCS, up to possible zero emissions, on the other hand.

Research on methane pyrolysis has intensified recently, documented by an increasing number of research groups in this promising field. To name a few, (i) the Montan University Leoben researches on a molten metal reactor using copper [93], (ii) the Netherlands Organization for Applied Scientific Research TNO patented a molten metal pyrolysis concept to produce hydrogen and carbon, in which liquid salt is used to separate the produced carbon from the molten metal [94], and (iii) the British company HiiROC, founded in 2019, filed several patent applications for its plasma methane pyrolysis system and is trying to bring its pilot-scale plant into operation by 2023. The systems will be designed as modular, scalable on-site units for different consumers [95].

Moreover, at this time, research is being undertaken on many other low-carbon hydrogen production processes, so this comparison can only be a snapshot of the three technologies discussed herein – water electrolysis (AEL, PEMEL, HTEL), SMR with CCS, and methane pyrolysis. In the future, other efficient low-carbon processes will have to be included in the comparison, such as the following technologies: (i) the RE-compatible and at the same time cost-effective polymer-alkali electrolysis, (ii) the HTEL, which can be operated as rSOC or in co-electrolysis mode, (iii) autothermal reforming with CCS, which will achieve capture rates of 95 % in the foreseeable future (2024) [38] and can therefore really be described as low-carbon compared to SMR-CCS (provided that the CO_2 is stored safely or used in processes that do not release it back into the atmosphere), (iv) the more efficient chemical looping process compared to SMR-CCS [35] and (v) the CO_2-neutral biogas reforming process.

5. Conclusion

In this low-carbon hydrogen production technology comparison, methane pyrolysis was found to be a promising alternative to water electrolysis and SMR with CCS.

All three low-carbon hydrogen production technologies have a wide range of TRL between 4 and 9, as each technology has less mature concepts (e. g., HTEL or thermal pyrolysis). Nevertheless, also commercial plants operate successfully in an industrial environment, e. g., the plasma pyrolysis of Monolith, SMR-CCS plants of Air Products, and several installed AEL.

Furthermore, by splitting methane into hydrogen and solid carbon, this endothermic reaction does not release any direct CO_2 emissions. If RE can be used for the required electricity demand, the CO_2 emissions of methane pyrolysis are relatively low. Compared to current blue hydrogen production facilities that cannot capture 100 % of the SMR process-related emissions, methane pyrolysis has a lower carbon footprint. Compared to electrolysis, plasma methane pyrolysis using RE can also reach net-zero emissions.

In terms of economics, methane decomposition ranges in the middle of electrolysis and SMR-CCS. Since pyrolysis-carbon emerges as solid carbon that can widely be used in several applications, it is a high-quality and important product. Assuming that 100 % of the carbon product can be sold, this results in less LCOH, making methane pyrolysis more attractive and competitive with the other two described hydrogen production options.

Concluding, the so-called turquoise hydrogen combines the advantages and disadvantages of the other two hydrogen technologies: relatively low LCOH, as for blue hydrogen, and nearly zero CO_2 emissions, as for water electrolysis. Thus, methane decomposition is considered another promising low-carbon hydrogen production technology that needs to be implemented alongside green and blue hydrogen to achieve the climate goals.

CRediT authorship contribution statement

Dermühl Sandra: Writing – original draft, Conceptualization, Investigation. **Riedel Uwe:** Writing – review & editing, 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.

Data availability

No data was used for the research described in the article.

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