

# Methane up-carbonizing: a way towards clean hydrogen energy?

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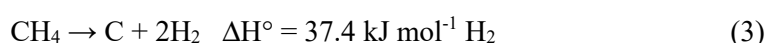
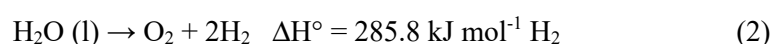
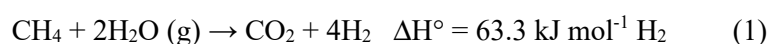
## Abstract

A global transition to a hydrogen economy requires widespread adoption of clean hydrogen energy. Methane cracking is one of the most viable technologies for producing clean hydrogen, nearing the ultimate zero-carbon-emissions targets. While major progress has been made in the lab-scale development of high-performance reactors and catalysts for methane pyrolysis, research focusing on industry-relevant scale and process conditions is in its infancy. Herein, recent advances in fundamental and applied research in methane pyrolysis are critically examined, focusing on physico-chemical mechanisms to achieve energy-efficient, low-carbon-emission, scalable processes. The highlighted recent efforts to bridge the gap between laboratory research and industrial applications reveal rapid advances in practical applications based on synergistic chemical engineering, catalysis, and materials science research.

Perspectives, challenges, and opportunities for translational research towards commercial applications of methane cracking are discussed aiming at clean hydrogen production.

## 1. Status

To achieve the ambitious CO<sub>2</sub> emissions reduction target based on the COP27 Egypt agreement, clean energy sources are vital to decarbonize the industrial and habitable environments. Hydrogen is one of the most promising zero-carbon energy vectors. It is used in fuel-cells to power vehicles and its uses in both industrial processes and domestic heating are rapidly emerging [1,2]. Several technologies for the production of clean hydrogen are currently in development and adoption [3–6]. Based on the environmental impact of the H<sub>2</sub> production approach, the various routes for hydrogen production have been associated with different color codes for easy identification as summarized in Figure 1(a). The present industrial hydrogen production pathway is still dominated by the steam methane reforming (SMR) process using fossil fuels (equations (1)) with unavoidable generation of huge amounts of CO<sub>2</sub>. The hydrogen produced via this route is referred to grey hydrogen. In the case where the SMR process is combined with CO<sub>2</sub> capture processes, grey hydrogen turns to blue hydrogen. Presently, carbon capture and storage (CCS) technology is still in its early stages and its environmental and geological impact still needs to be addressed. Water electrolysis powered by renewable energy (equations (2)) is a promising way to produce clean hydrogen and the produced hydrogen is known as green hydrogen. Methane pyrolysis (also known as methane cracking or methane dissociation) is another approach for clean hydrogen production, which ideally produces gaseous H<sub>2</sub> designated as turquoise hydrogen and solid carbon (equations (3)). Based on the energy source used and the feedstock, the hydrogen color can be assigned as pink, aquamarine and brown as well [7].



As noted from equation (1)-(3), the energy requirement for turquoise hydrogen produced via the pyrolysis of methane ( $\Delta\text{H}^\circ = 37.4 \text{ kJ mol}^{-1} \text{ H}_2$ ) is much smaller than that of water electrolysis ( $\Delta\text{H}^\circ = 285.8 \text{ kJ mol}^{-1} \text{ H}_2$ ) and the SMR process ( $\Delta\text{H}^\circ = 63.3 \text{ kJ mol}^{-1} \text{ H}_2$ ). It is important to note

that the carbon footprint of water electrolysis powered by non-renewable energy is even larger than that of the SMR process because of the high energy consumption. Al-Qahtani et al. [4] made a comprehensive assessment of a wide range of promising H<sub>2</sub> technologies considering resource depletion, levelized cost of hydrogen and environmental externalities simultaneously (impacts on ecosystem quality and human health) as shown in Figure 1(b). Methane pyrolysis emerges as the most promising technology for a low-carbon and affordable hydrogen production. Parkinson et al. [8] have also compared and evaluated 12 different H<sub>2</sub> production routes as shown in Figure 1(b) and their results suggest that methane pyrolysis may be the most cost-effective technique in the short-term that encourages the construction of infrastructure required to sustain a high penetration of hydrogen in the energy sector. At present, worldwide hydrogen production stands at approximately 120 million tons (Mt) annually, with two-thirds of this volume being pure hydrogen and the remaining one-third mixed with other gases. Nevertheless, to satisfy just 5% of our global energy demands, as per the 2021 data, we would need to produce a staggering 188 million tons (Mt) of hydrogen [9]. Despite the critical need to reduce greenhouse gas emissions, fossil fuels are still expected to have a dominant share of the global energy demand up to 2050 [10]. Methane pyrolysis represents a promising alternative for low-carbon hydrogen production to address the energy transition and the ongoing environmental degradation [11–13].

Numerous comprehensive reviews have been published, offering in-depth insights into methane pyrolysis for hydrogen production [12–20]. Significant amount of the analyzed data pertains to the laboratory-scale exploration of high-performance reactors and catalysts in both thermal non-catalytic and catalytic methane cracking processes. Recently, McConnachie et al. [14] and Msheik et al. [21] have provided detailed and up-to-date analyses, particularly focusing on liquid catalysts. However, it is important to note that research focusing on scaling-up and process conditions relevant to industry for diverse methane pyrolysis technologies is in its infancy. This perspective-type article seeks to provide a broad overview of the current state of this field, with a specific emphasis on its present status and an exploration of the fundamental aspects across various methane pyrolysis technologies. Additionally, it outlines the existing limitations and foresees the forthcoming engineering challenges in the practical implementation of this technology. In doing so, it serves as a valuable resource for researchers and practitioners involved in both foundational studies and industrial applications. This perspective-type review is anticipated to be particularly advantageous for individuals interested in the latest research developments in this domain, drawing perspectives from both academic and industrial sectors.

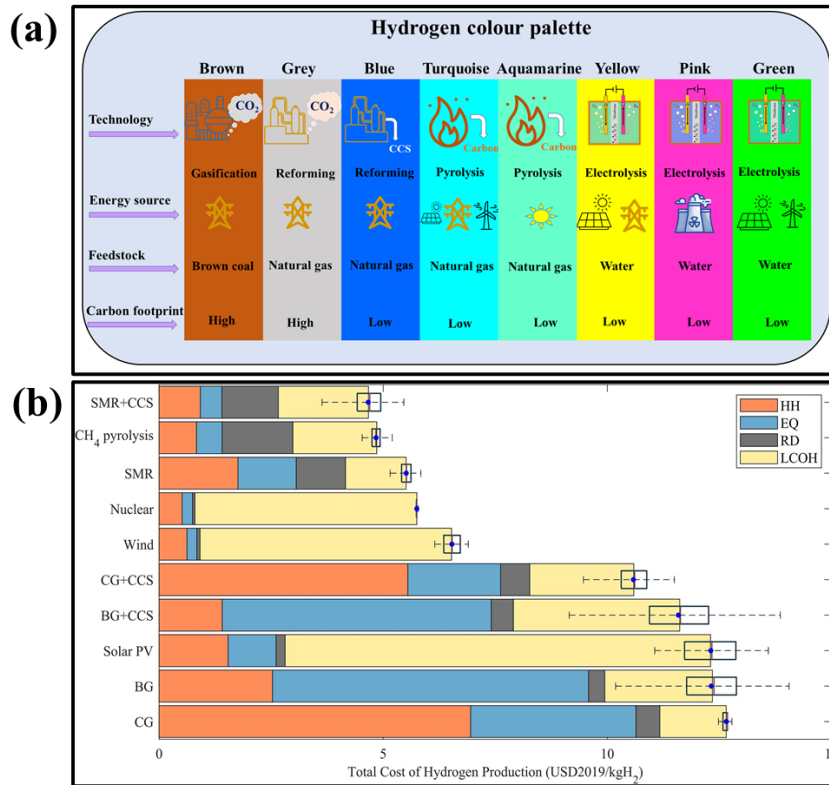


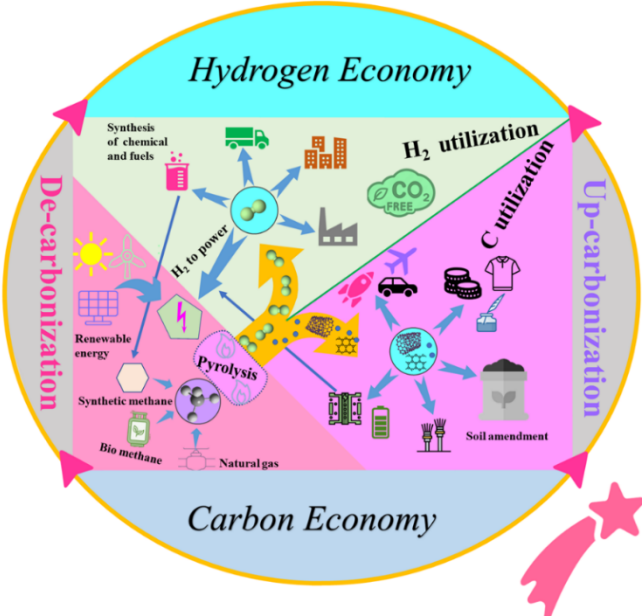
Figure 1. (a) Hydrogen color coding of various approaches for hydrogen production; (b) Total cost of the evaluated H<sub>2</sub> production routes in terms of externalities (HH, EQ, and RD) and LCOH (Reprinted with permission from [3]). HH refers to the monetized human health indicator, EQ stands for the monetized ecosystem quality indicator, RD stands for the monetized resources depletion and LCOH stands for the levelized cost of hydrogen. The other acronyms in Figure 1(b): SMR: Steam methane reforming; CCS: Carbon capture and storage; CG: Coal gasification; BG: Biomass gasification; PV: Photovoltaics.

## 2. Up-to-date progress

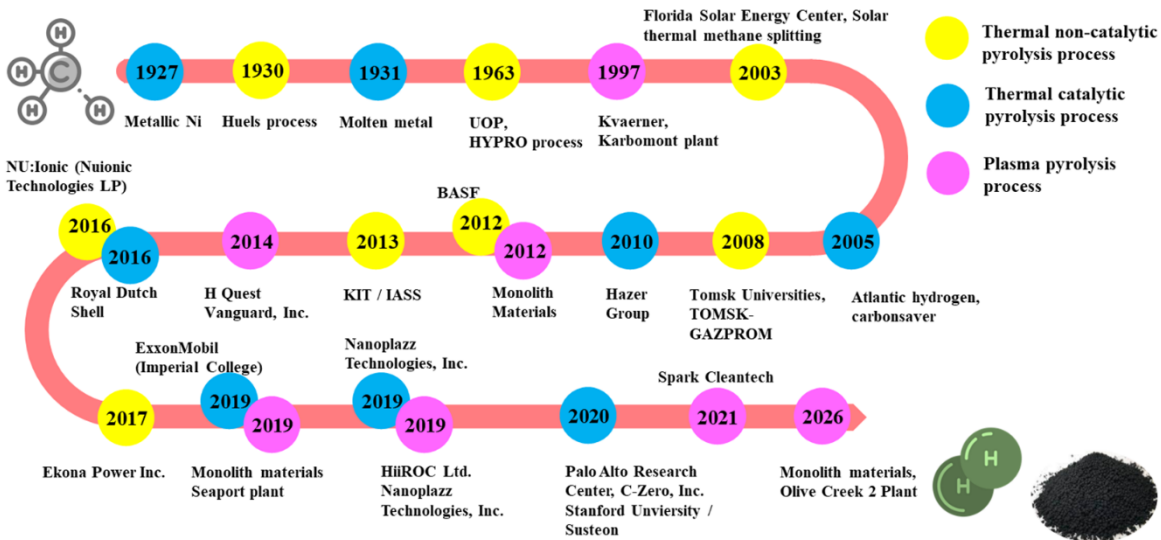
Apart from natural gas, the source of methane used can also be biomethane (derived from plant-derived materials) and synthetic methane (derived from CO<sub>2</sub> utilization). In particular, hydrogen production from biomethane can be carbon-negative even using the current electricity energy sources. The H<sub>2</sub> produced by methane cracking can be stored and transported safely over long distances using the liquid organic hydrogen carrier technologies and can then be used as a chemical feedstock or fuel in buildings, transportation, power generation, and industry (Figure 2(a)). Methane pyrolysis research has been going on for over a century and different types of reactors have been considered and studied (Figure 2(b)), but the technology has yet to be commercialized. The major technologies or routes for methane cracking can be generally

grouped into three categories [22] as shown in Figure 2(c): thermal non-catalytic pyrolysis, thermal catalytic pyrolysis, and plasma pyrolysis. In the following, the various routes are critically examined, focusing on the current status and insights, as well as the challenges and opportunities for fundamental research and industrial translation.

(a)



(b)



(c)

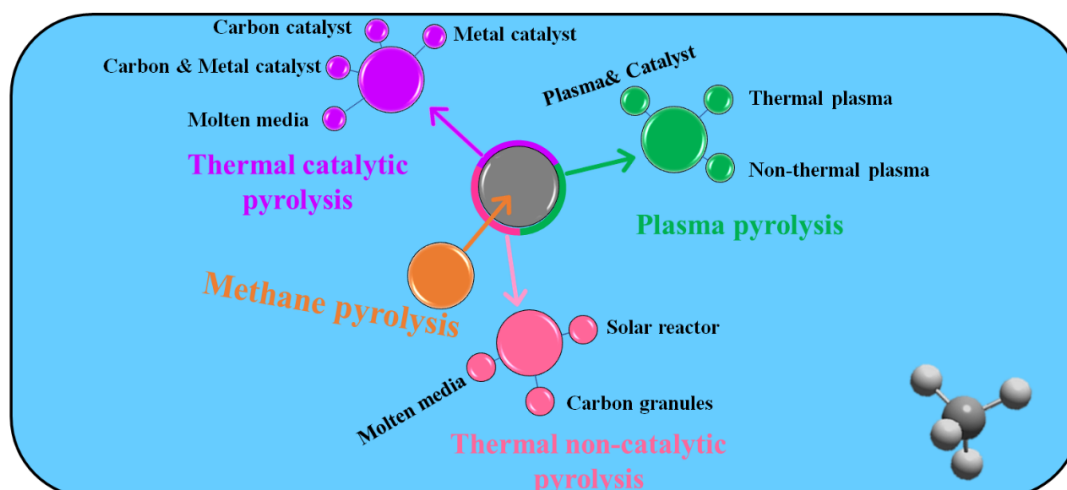


Figure 2. (a) Schematic representation of hydrogen and carbon product productions via methane pyrolysis and of their utilizations; (b) Key developments in methane pyrolysis and (c) Common classification of methane pyrolysis routes.

## 2.1. Thermal non-catalytic pyrolysis process

Methane dissociation is an endothermic reaction that typically occurs at high temperatures. To achieve a reasonable high conversion in a thermal non-catalytic pyrolysis process, more than 1200 °C is required to cleave the C-H bonds of CH<sub>4</sub> [23]. A thermal non-catalytic decomposition of natural gas process at temperatures of up to 1400 °C has been developed by a consortium led by BASF [22]. Currently, the ongoing research project is focused on enhancing and scaling up the thermal non-catalytic pyrolysis process, building upon the information provided in a 2021 BASF report [24]. The high-temperature requirement of the non-catalytic methane pyrolysis process can also be reached by utilizing concentrated solar energy, which can be considered as a sustainable and promising route for hydrogen production [7,21,25,26]. The solar reactor concepts developed by different research groups have shown significant recent progress [25,27–29]. Although higher methane conversions have been achieved, the issue of carbon deposition clogging the solar reactors remains. This problem also persists in conventional thermal reactors and inhibits the continuous operation of the pyrolysis process. With this problem in mind, better reactor designs to address the coking issue and achieve homogenous heating, are needed. As of the date of this publication, scaling up of the solar processes for methane cracking at high temperatures remains a big challenge. Moreover, a very high sunlight concentration is needed to reach the high temperatures (>1200 °C), which requires large-scale solar power concentrators. The required high temperature in solar systems can be reduced with the addition of catalysts.

Thus, custom-designed solar systems which are compatible with the catalysts, are needed. The reduced process temperature also allows for the use of lower-cost materials in the construction of the solar reactor.

## **2.2. Thermal catalytic pyrolysis process**

The reaction temperature required for the decomposition of CH<sub>4</sub> can be significantly reduced in the presence of a catalyst. Catalytic methane decomposition has attracted considerable attention and been extensively investigated over a variety of metal-based and carbonaceous catalysts [15,16,33,18–21,26,30–32]. The catalytic performances towards methane decomposition are determined by the properties of the different catalysts such as supports, promoters, shape, and size. Transitional metals like iron, nickel and cobalt are the most widely studied catalysts because of their availability, high performance, and low cost. Ni shows excellent performance for catalytic methane cracking and is one of the most catalytically active transition metals. Fe-based catalysts tend to be more cost-effective, but they generally operate at higher temperatures compared to than Ni- based catalysts. However, rapid encapsulation of active sites by the produced solid carbon deactivates Ni metal catalysts quickly, particularly at high temperatures. A wide range of supports and promoters have been employed for enhancing the catalytic performance and resistance to deactivation of the metal catalysts [18,34,35]. The most widely used supports are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO, MoO, TiO<sub>2</sub> and MgO. Numerous alternative strategies have been explored to enhance the design of methane decomposition catalysts for more efficient and sustainable hydrogen production. These strategies encompass the incorporation of secondary or tertiary metals, utilization of various synthesis methods, and modifications to the support material, all of which have been extensively examined and discussed in the literature [16,21,36–39]. Guevara et al. [40] investigated the catalytic decomposition of CH<sub>4</sub> using a nickel/MCM-41 catalyst with Ce and observed no major catalytic deactivation after 1400 min, which can be linked to the ordered pore system and large surface area of the MCM-41 support. Although great progress has been achieved for catalytic decomposition of CH<sub>4</sub> via the use of different types of catalysts and the optimization of the process conditions, the accumulation of the carbon produced on the catalyst surface remains the main challenge leading to gradual catalyst deactivation. To maintain the process continuity, the catalysts require periodic removal of the accumulated carbon through a regeneration process: gasification (with CO<sub>2</sub> or steam) or oxidation (with air or oxygen). Once the catalysts are deactivated, the input stream can be directly switched from CH<sub>4</sub> to the regeneration gas, which removes the deposited carbon from the surface of the catalysts, regenerating the catalysts. However, the regeneration cycles can result in a reduction in the performances of the catalysts

over time due to the oxidation of the active sites (such as Ni agglomeration) and undesirable CO<sub>2</sub> emissions based on the reported studies [16,21,26]. Since the produced carbon reacts during the regeneration processes, the potentially useful carbon product from pyrolysis is lost. In terms of CO<sub>2</sub> emissions, this catalyst regeneration approach cannot be a promising route towards CO<sub>2</sub>-free H<sub>2</sub> production.

To address the catalyst deactivation issue, using the carbon itself as a catalyst for methane cracking to combat the issue of carbon poisoning has attracted major attention. Different types of carbon-based materials have been studied as catalysts for the catalytic methane pyrolysis process, including activated carbon, ordered mesoporous carbons, carbon black, carbon nanotubes, activated carbon, graphite and coal chars [15,16,21,26,30,41]. In spite of carbon catalysts showing excellent stability for high-temperature operations, undergoing deactivation is ultimately unavoidable just as with metal-based catalysts.

In general, Ni-based catalysts show a better activity while Fe-based and carbon-based catalysts show better stability. Regarding the environmental concerns, there is a compelling case for the adoption of Fe-based and carbon-supported catalysts, with a particular focus on the future utilization of the resulting solid carbon products. Importantly, addressing the challenge of catalyst regeneration without CO<sub>2</sub> formation still represents a major hurdle in advancing the catalytic methane pyrolysis process. Thorough techno-economic analyses are essential to bridge the knowledge gaps that impede the scaling up the thermal catalytic pyrolysis of methane.

Recently, focus has been set on using molten media (molten metals and salts) for methane cracking at low reaction temperatures [42–49], these processes represent a promising path for continuous H<sub>2</sub> production. In contrast with the conventional fixed catalyst bed reactor, the methane bubbles dissociate with the high temperature of molten media and the produced carbon particles float on the surface of the molten media, preventing catalyst deactivation and reactor blockages due to carbon clogging. Different types of molten metals or salts have been investigated as a catalytic material or heat transfer medium. The improvement of heat transfer, as a result of the high heat capacity of molten metals or salts, and the enhancement of the residence time of methane gas owing to the liquid viscosity resulted in a high methane conversion as well as granting reactor protection from thermal shocks. A wide variety of metal alloys formed by the low-melting-point metals have been investigated for use as molten media [42] in CH<sub>4</sub> cracking and it has been reported that a Ni<sub>0.27</sub>–Bi<sub>0.73</sub> molten alloy achieved the highest methane conversion (95%) among all the studied metal alloys at 1065 °C. In a recent study, they have developed a new Cu<sub>0.45</sub>Bi<sub>0.55</sub> alloy and achieved a surprisingly high activity, showing a higher catalytic performance than that of the Ni<sub>0.27</sub>Bi<sub>0.73</sub> molten alloy [44]. Recently,



Chen et al. introduce a novel and exceptionally effective catalyst obtained through the alteration of a Ni-Bi liquid alloy, with the incorporation of Mo to form a ternary NiMo-Bi liquid alloy catalyst [49]. This catalyst demonstrated a notably low activation energy of 81.2 kilojoules per mole, facilitating methane pyrolysis within the temperature range of 450 to 800 °C. Remarkably, the catalyst displayed both 100% selectivity for hydrogen and impressive stability for up to 120 hours at 800 °C.

This finding demonstrates new ideas for utilizing catalytically inert and low-cost metals to improve the performance of the molten alloy for methane cracking. Despite the large merits provided by the molten metals for CH<sub>4</sub> cracking over conventional pyrolysis, the metal losses and carbon contamination caused by the metal evaporation due to the high vapor pressure pose big challenges.

The marketability and practicality of carbon products generated through molten media depend on morphology, quality, and contamination levels, necessitating additional separation procedures as a final step. Plamer et al. [50] observed a surprisingly high degree of metal contamination from the produced carbon collected after 120 hours of experiments using 27 mol % Ni–73 mol % Bi. To purify the resulting carbon, three distinct methods were evaluated, including vacuum distillation, magnetic extraction, and hydrochloric acid washing. The highest achievable carbon purity reached 97.8 wt%, but only after implementing multiple cleaning and separation processes the metal contamination levels decreased to 0.2–2 wt% [50]. These levels and the associated additional costs required to attain them are likely unacceptable in a commercial production process. Carbon generated through the commercial pyrolysis process should ideally be free of contamination, as even a trace of residual metal content would make it unsuitable for sale or safe disposal. Molten salts with lower vapor pressure and melting points can be a promising alternative to molten metals [14,51]. Separating the molten salts from the contaminated carbon is much easier than from molten metals since the salts are soluble in water. Molten salts generally show low catalytic performance thus coupling molten metals with salts may reach high performances for methane pyrolysis with a robust system against deactivation [21,52]. Despite significant advancements made through various methods to enhance the purification of the resulting carbon, the achieved level of purity still falls short of meeting commercial standards according to the literature [32,53–55]. An area that demands further consideration in the future is the development of effective methods for the continuous removal of carbon particles accumulated on the surface of molten media. It is also important to select appropriate salts and metals that are not prone to introducing contaminants. Methane pyrolysis within molten media represents a relatively new approach, and extensive research is needed to

identify suitable combinations and to optimize the process conditions suitable for future industrial applications.

Currently, Hazer Group Ltd. is one of the market leaders in catalytic methane decomposition for H<sub>2</sub> production, employing a fluidized bed reactor operating at 850 °C in the presence of iron ore catalysts. The technology is currently still at the pilot scale. Despite its promising potential, thermal catalytic pyrolysis of methane still requires further development to improve H<sub>2</sub> production. Furthermore, the disposal of substantial quantities of catalysts presents a significant challenge for large-scale application. Therefore, extensive investigations must be undertaken to address the knowledge gaps hindering the advancement of large-scale H<sub>2</sub> production through thermal catalytic pyrolysis of methane.

### **2.3. Plasma pyrolysis (thermal/non-thermal) process**

Plasma, known as the fourth state of matter, is an ionized gas and consists of a variety of reactive species including energetic electrons, excited atomic and molecular species, photons, reactive radicals, and ions [56]. In general, the plasma used for methane pyrolysis can be categorized as thermal and non-thermal plasmas. In most cases, plasma processes operate in the absence of a catalyst. One of the fundamental parameters that characterizes a plasma is the temperature of the plasma species. The temperatures of the electrons, gas molecules and ions in a thermal plasma are homogeneously distributed. On the other hand, the electrons have a much higher energy compared with the energies of gas molecules in a non-thermal plasma, which can provide efficient and fast heat transfer to accelerate thermodynamically unfavorable chemical reactions. Many plasma systems for methane cracking have been developed and the outstanding merits of the plasma pyrolysis process are the fast switching-on and shutting-off of the systems allowing for flexible utilization of the intermittent and irregular electricity supply of the renewable energy sources such as solar and wind energies [57–60].

Thus far, thermal plasma-based methods represent the most highly developed commercialized technology for the production of H<sub>2</sub> and carbon black, which were pioneered by Kvaerner and SINTEF. However, the carbon black quality produced by this technology was deemed inadequate, and as a result, it was discontinued in 2003. Nonetheless, Monolith Materials is still advancing the technology through IP licensing agreements. The plasma torch technology is based on the SINTEF/Kvaerner torch concept but with many modifications and improvements, where producing carbon black is the primary product, and the working temperature is 1000-3000 °C. Monolith Materials has also announced plans to construct a

275,000 t/y carbon-free anhydrous ammonia plant in Hallam, Nebraska, USA, to process the hydrogen produced through methane cracking [61]. The ammonia product is aimed at the local fertilizer market. Due to the high operating temperature, thermal plasma processes generally have a high energy consumption, and the energy efficiency is low because of the thermal losses. To achieve an efficient methane conversion, more than 30% of the energy input is needed to exceed the theoretical thermodynamic value [62].

Non-thermal plasma processes have gained increasing attention since they can be operated at a low gas temperature while still providing high electron temperatures, improving the energy efficiency and reducing the investment needed for the equipment to cope with the harsh conditions at high temperatures [63–66]. Several types of non-thermal plasma have already been investigated for methane decomposition including microwave (MW) plasma, dielectric barrier discharge (DBD), gliding arc (GA), corona and spark discharges. Gallon et al. reported the production of carbon nanofibers on a NiO/Al<sub>2</sub>O<sub>3</sub> catalyst, achieving a 99% hydrogen selectivity during plasma methane activation using a DBD reactor [67]. Heijkers et al. [68] investigated the underlying reaction mechanisms of methane decomposition via chemical kinetics modeling in the case of MW, DBD and GA reactors and discovered that thermal effects have a major role in the methane conversion whereas vibrational–translational non-equilibrium play a minor role. The Gazprom (Russian Federation) company is a typical example that is currently involved in the non-thermal plasma technology for methane pyrolysis. They patented a method of combining a nickel-based catalyst stage with a plasma torch [69]. So far, there has been no published approach to scaling up the laboratory apparatus, and the technology remains at the laboratory scale. Despite significant efforts to develop a non-thermal plasma process for methane cracking with a high energy efficiency, the conversion efficiency of methane via the non-thermal plasma process remains low.

One of the major challenges in operating a plasma reactor for hydrogen production is the formation of carbon deposits in the electrode surfaces or the reactor wall over time, which tends to quench the plasma and thus halt the process. Moreover, the majority of investigations in the literature use diluted methane with inert gases such as N<sub>2</sub>, Ar, and He. More investigations are needed to run pure methane or methane-rich gas as an input in the case of using non-thermal plasma. Noteworthy, the plasma processes can operate either under low or atmospheric pressure conditions. Therefore, the production of hydrogen at low or atmospheric pressures requires additional energy which will increase the overall cost of the compressed hydrogen storage.

### 3. Summary

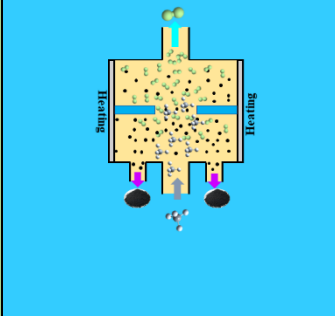
### 3.1. Technology readiness

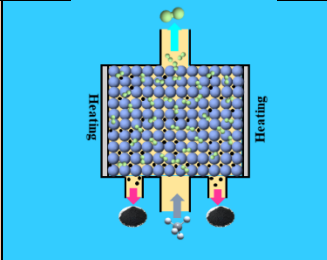
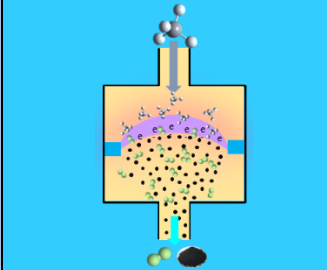
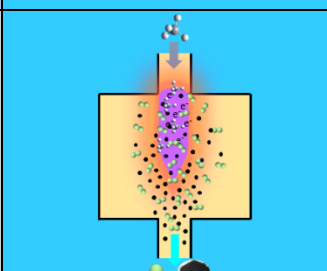
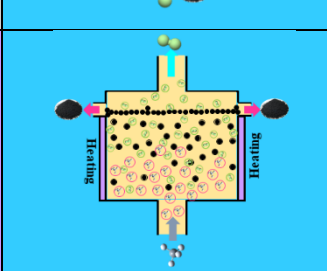
According to the currently available information, the technology landscape for methane cracking is fragmented, with no clear winner. The different methane pyrolysis processes for H<sub>2</sub> production have distinct advantages and drawbacks, which are summarized in Table 1. The plasma pyrolysis process developed by Kvaerner and Monolith Materials is particularly promising, with high commercialization potential. Other pyrolysis technologies (thermal non-catalytic pyrolysis, thermal catalytic pyrolysis, molten metal/salt process) are still at the laboratory scale or the pilot-scale and it is unlikely that they will reach the commercial-ready level in the next few years.

### 3.2. Lower process temperatures needed

The reaction temperature ranges for methane pyrolysis in various pyrolysis processes (molten media-based, non-catalytic including plasma-based, carbon-based and metal-based catalyzed reactions) are partially overlapping. Figure 3 (a) presents the methane conversion as a function of the reaction temperature in different pyrolysis processes. The approximate temperature ranges acceptable for each reaction type are generally summarized as follows: 550–800 °C for Ni-based catalyzed reactions, 550–700 °C for Co-based catalyzed reactions, 700–1100 °C for molten media-based pyrolysis processes, 600–900 °C for Fe-based catalyzed reactions, 750–1100 °C for carbon-based catalyzed reactions and above 1100 °C for the non-catalytic reactions. As shown in Figure 3(a), the CH<sub>4</sub> conversion rate can generally reach close to 100% at temperatures above 1200 °C in the case of thermal non-catalytic and plasma pyrolysis processes, whereas it seems that methane is difficult to completely convert into hydrogen via the thermal catalytic pyrolysis process (including the cases using molten media).

Table1. Overview of different methane pyrolysis routes

| CH <sub>4</sub> pyrolysis routes | Advantages  | Disadvantages   | Typical Example | TRL | Typical reactor   |
|----------------------------------|---|---|-----------------|-----|---|
| Thermal non-catalytic process    | <ul style="list-style-type: none"> <li>-No deactivation</li> <li>-Carbon product with high purity (~100% at high temperature)</li> <li>-High conversion (~100%)</li> <li>-Potential to perform at high pressures</li> </ul> | <ul style="list-style-type: none"> <li>-Inhomogeneity</li> <li>-Low heat efficiency</li> <li>-High temperature</li> </ul> | -BASF           | 4   |  |

|                              |  |  |  |       |   |
|------------------------------|--|--|--|-------|---|
| Catalytic process            | <ul style="list-style-type: none"> <li>-Lower temperature</li> <li>-Material of construction</li> <li>-Scalability</li> <li>-Potential to perform at high pressures</li> </ul>     | <ul style="list-style-type: none"> <li>-Carbon products with impurities</li> <li>-Catalyst deactivation</li> <li>-Catalyst cost, inserting</li> </ul>              | <ul style="list-style-type: none"> <li>-BASF</li> <li>-Hazer Process</li> </ul>                  | 4 - 6 |    |
| Plasma process (thermal)     | <ul style="list-style-type: none"> <li>-Fast switch on/off</li> <li>-High conversion</li> <li>-No sensitive cooling</li> <li>-No catalyst needed (in most of the cases)</li> </ul> | <ul style="list-style-type: none"> <li>-Low energy efficiency</li> <li>-High temperature</li> <li>-Broad carbon quality</li> <li>-Low energy efficiency</li> </ul> | <ul style="list-style-type: none"> <li>-Monolith materials</li> <li>-Kvaerner process</li> </ul> | 8 - 9 |    |
| Plasma process (non-thermal) | <ul style="list-style-type: none"> <li>-Fast switch on/off</li> <li>-No sensitive cooling</li> <li>-Low temperature</li> <li>-High energy efficiency</li> </ul>                    | <ul style="list-style-type: none"> <li>-Broad carbon quality</li> <li>-Low conversion</li> </ul>   | <ul style="list-style-type: none"> <li>-Atlantic Hydrogen</li> <li>-Gazprom</li> </ul>           | 4     |   |
| Molten metal/salt process    | <ul style="list-style-type: none"> <li>-No blocking</li> <li>-Catalytic function</li> <li>-Good heat transfer</li> </ul>   | <ul style="list-style-type: none"> <li>-Carbon products with impurities</li> <li>-Loss of metals/salts</li> <li>-Corrosion</li> </ul>                              | <ul style="list-style-type: none"> <li>-TNO-EMBER process</li> <li>-C-Zero</li> </ul>            | 3 - 4 |  |

### 3.3. Up-carbonization

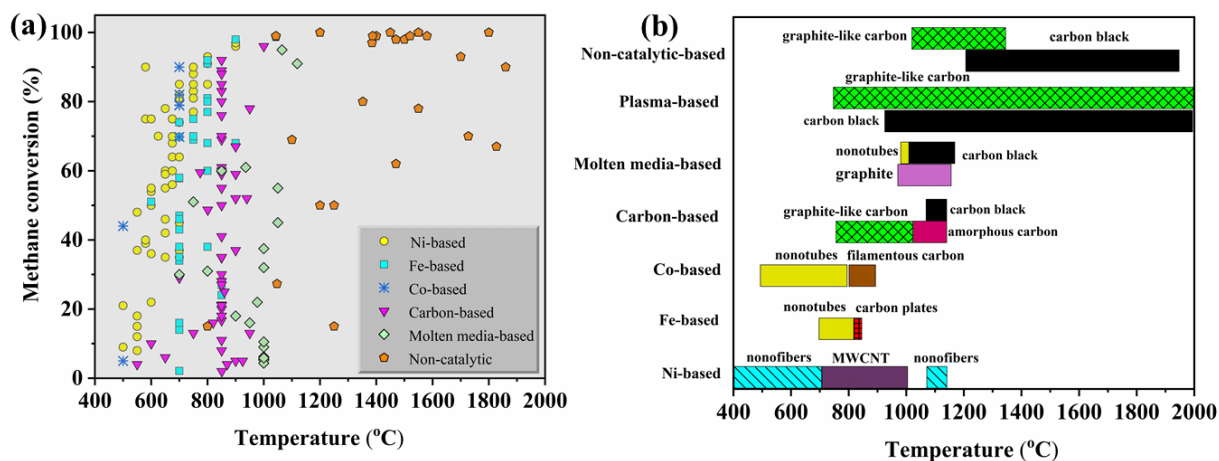
The quality and applications of the carbon produced are also critical for increasing the economic efficiency of the methane pyrolysis process. As noted from Figure 4, the global demand for carbon black was nearly 16.4 million metric tons (MMT) by 2022 and will continue to increase for soil amendment and environmental cleanup [70] in the near future. The continued development of methane pyrolysis technologies that create high-value forms of carbon, such as carbon nanotubes, is also critical for successful commercial implementation since carbon nanotubes are increasingly used in the production of lithium-ion batteries for renewable energy storage. The reaction conditions have a significant influence on the

morphology of the carbon produced. Based on published literature results [17,21,35,42], Figure 3(b) depicts a simplified representation of the main type of carbon product obtained from the various methane pyrolysis routes (using different types of catalysts) as a function of the reaction temperature. In the thermal catalytic pyrolysis process, metal-based catalysts tend to produce filamentous carbon products such as carbon nanotubes (CNTs) and nanofibers, whereas carbon-based catalysts generate primarily graphite-like carbon or carbon black. Carbon formation in molten media differed significantly from conventional catalytic pyrolysis over solid catalysts. Carbon atoms are solubilized as methane cracking in molten media, which frequently prevents the formation of filamentous carbon products. In some cases, such structures can still be obtained through pyrolysis such as using Ni–Bi/salt (KBr or NaBr) [52]. Thermal non-catalytic and plasma methane cracking techniques yield mostly amorphous carbon or graphite-like carbon, similar to carbon catalyzed methane decomposition. Based on the findings of the literature review and the goal of producing hydrogen [30,63], a thermal non-catalytic or plasma pyrolysis reaction may be a viable route to CH<sub>4</sub> decarbonation because it avoids the limitations and difficulties associated with catalysts, as well as the need for separation and purification units (membrane technology [71,72]) for pure H<sub>2</sub> production.

### 3.4. Mechanisms

Despite being the simplest hydrocarbon, the mechanisms of methane cracking reaction are still unclear. Since the 1960s, researchers have devoted efforts to investigate and postulate reaction mechanisms for thermal non-catalytic methane cracking (Figure 3(e)) [73]. Regardless of whether the produced carbon from the decomposition of CH<sub>4</sub> has a catalytic effect, the mechanisms of the reactions at lower and higher temperatures are quite different. At higher temperatures (> 1200 °C), thermal decomposition of methane occurs very quickly. A free radical mechanism generally explains the formation of H<sub>2</sub> and carbon. However, the carbon formation and the following steps (which result in a higher conversion rate) are not yet fully understood [74]. According to the findings of the literature review [74,75], at lower temperatures (< 1400 °C), methane is decomposed into a methyl radical and a hydrogen atom, whereas at higher temperatures (>1400 °C), methane appears to be dissociated into a hydrogen molecule and methylene. The reaction mechanisms of catalytic decomposition of methane have been studied and discussed in many works [15,16,18,34,73,76]. Dissociative adsorption mechanism and molecular adsorption mechanism are the widely accepted ones at present (Figure 3(d)). Methane is first adsorbed on the catalyst surface and then dissociates in a series of stepwise surface dehydrogenation reactions (the four C-H bonds in the adsorbed CH<sub>4</sub> molecule are decomposed gradually) via the molecular adsorption mechanism. The only

difference in the case of the dissociative adsorption mechanism is that methane directly dissociates upon adsorption on the active sites of the catalysts generating chemisorbed H and methyl radicals. Although various rate-limiting steps for thermal catalytic methane pyrolysis have been proposed, the reaction mechanism and overall rate-limiting step remain an open question. The final carbon product's morphology is closely linked to the catalyst's itself characteristics, which can sometimes influence the overall rate-limiting step. In the case of plasma pyrolysis of methane, it is well accepted that the collisions of electrons with methane molecules cause electron impact reactions such as ionization, excitation, dissociation, and so on. H and CH<sub>x</sub> (x = 1, 2, 3) radicals are the major species which could initiate the secondary reactions. According to the proposed reaction pathway in Figure 3(c), the majority of the CH<sub>x</sub> radicals in the plasma active zone participate in the dissociation reactions that generate hydrogen radicals and gaseous carbon. The remaining CH<sub>x</sub> radicals play an active role in post-plasma zone reactions to generate C2 hydrocarbons [68,77]. When gaseous carbon nucleates and aggregates on the electrode surface and reactor wall, solid carbon forms. H radicals generate H<sub>2</sub> primarily through H recombination. Combining in-situ characterization techniques with machine learning and modeling could be a promising way to elucidate the reaction mechanism of methane pyrolysis and identify the rate-determining step, which could lead to the development of high-performance catalysts and reactors.



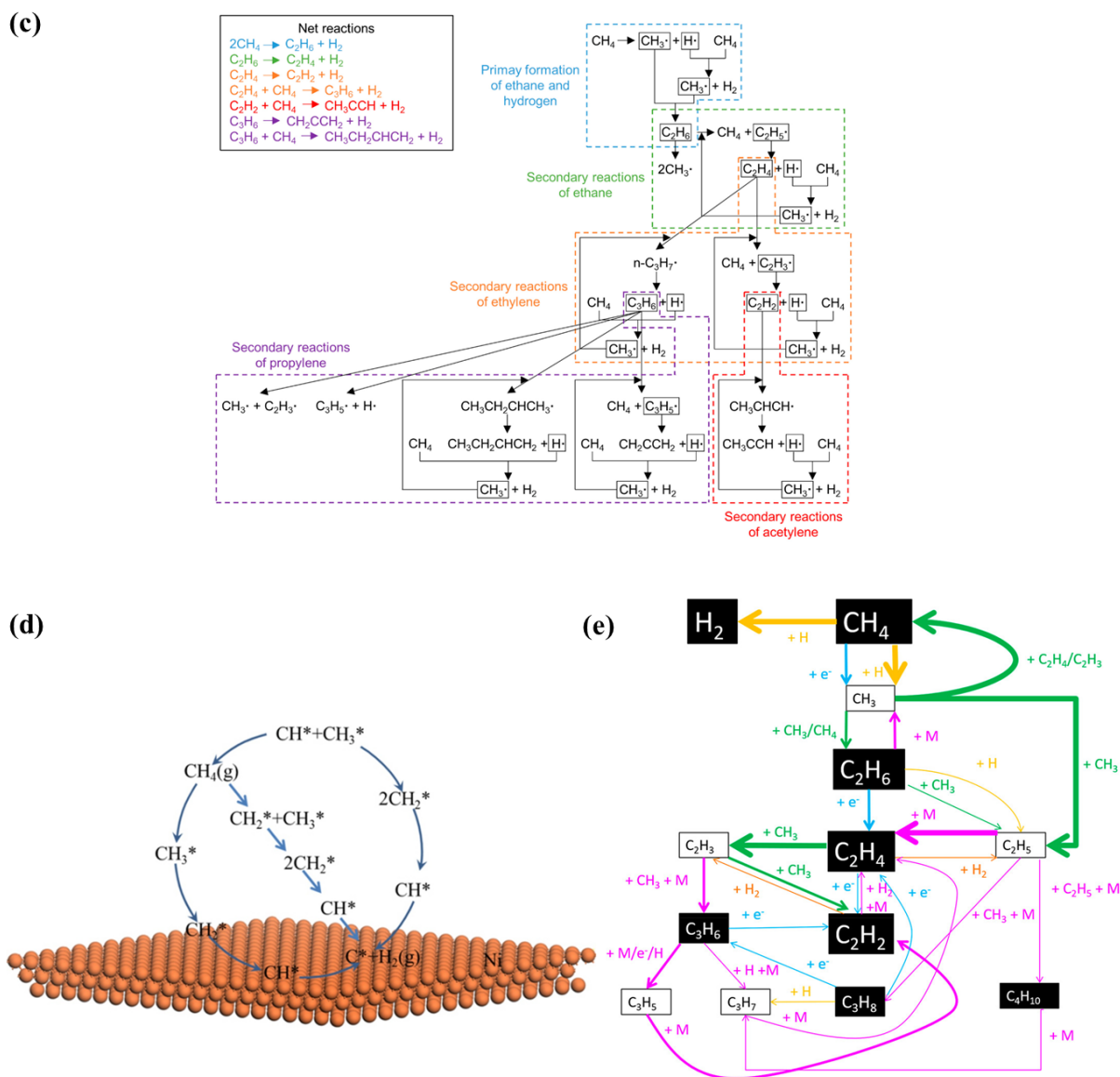


Figure 3. The methane conversion (a) and the primary carbon products obtained (b) as a function of reaction temperature in various pyrolysis processes. The data for the primary carbon products is mainly based on the information from [16,17,21,35]. Proposed reaction pathways for (c) thermal non-catalytic (Reprinted with permission from [15]), (d) thermal catalytic and (e) plasma-based (Reprinted with permission from [68]) methane pyrolysis.



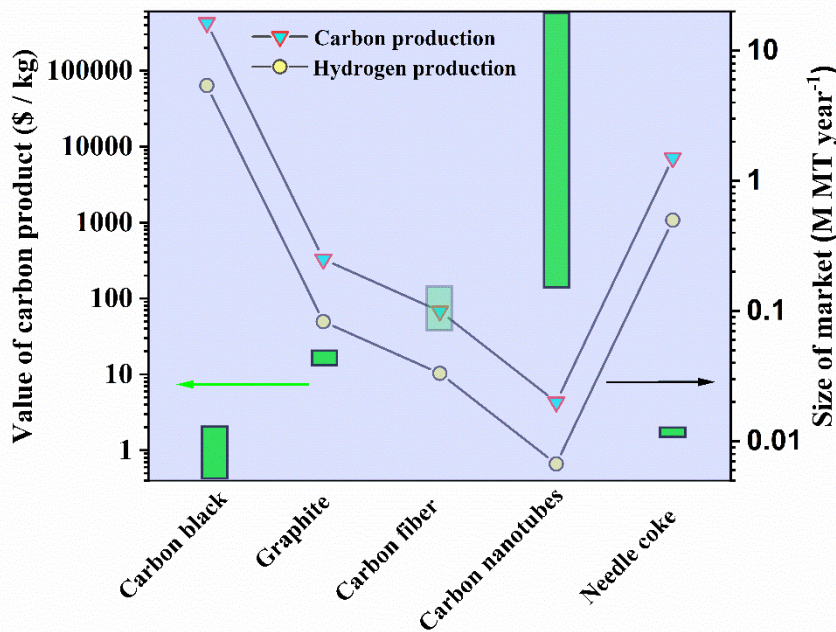


Figure 4 Carbon Products- Value and global market size (million metric tons (MMT)) based on the data from [78].

#### 4. Challenges, research needs, and opportunities

##### 4.1. Urgency and Innovation

Generally, methane pyrolysis has a promising future as a CO<sub>2</sub> free hydrogen production technique. Nonetheless, there are still many challenges and open questions regarding its industrial implementation. At present, methane decomposition is mostly associated with pyrolysis of natural gas for H<sub>2</sub> production. The use of real-world natural gas for large-scale H<sub>2</sub> production should take into account the impact of the impurities such as higher hydrocarbons. CH<sub>4</sub> emissions from natural gas production is an important consideration [79–81] and should not be underestimated when promoting it with technologies like methane pyrolysis to lessen the impact of climate change. Given the impending deadline for achieving the net zero goal, it is imperative to prioritize this technique as a hydrogen production technology for expediting the transition. This recognition becomes even more significant in light of the ambitious decarbonization goals outlined in the 'Egypt Climate Pact.' Further issues such as hydrogen storage, distribution, and end-use might well deserve intensive work on the basis of the green chemistry concept for the development of the hydrogen economy. In addition to temperature, residence time and pressure are also important operating parameters for methane pyrolysis. Special consideration should be given to the impact of high pressure because operating at high

pressure could be of special importance in reducing reactor volume at industrial scale, whereas most reported works generally run at atmospheric pressure. Despite extensive efforts having been devoted to investigate the reaction mechanisms of methane cracking, no definitive conclusions on the elementary reactions and the rate-limiting step have been reached, requiring further investigations to get a better understanding of the reaction pathways.

*In-situ* characterization techniques offer the unique ability to observe and understand reaction kinetics and the formation of intermediate species in real-time during the methane pyrolysis process. These real-time monitoring methods play an important role in identifying the diverse reaction pathways and intermediate species involved in methane pyrolysis. This knowledge is crucial for the fine-tuning of reaction parameters and the design of efficient and durable catalytic materials that can selectively enhance the desired pathways, thereby enhancing the overall efficiency of hydrogen production. Numerical simulations also provide a powerful tool for predicting the behavior of the methane pyrolysis systems under a broad range of process conditions, some of which may be impractical or even impossible to explore through experimentation. Such simulations can effectively streamline the selection of potential catalysts and operating conditions, thereby expediting the discovery of novel catalysts and process enhancements. This focused approach enhances the chances for successful experimental validation and cost-effectiveness of the practical process development. Furthermore, the formulation and implementation of advanced mathematical models for methane pyrolysis is crucial. These models enable the comprehensive optimization of the entire production process, including reactor design, operating parameters, and integration with other systems such as renewable energy sources or carbon capture technologies [82,83]. This approach also facilitates the scaling up of laboratory-scale processes to industrial levels, a critical step for ensuring the efficient and cost-effective H<sub>2</sub> production. Collectively, *In-situ* characterization and numerical approaches are expected to substantially contribute to the development and advancement of next-generation H<sub>2</sub> production processes that are more energy efficient, economically viable, and environmentally sustainable.

The sale of the different solid carbon products produced from methane cracking can offset a significant portion of the cost of hydrogen. Figure 4 depicts the value and global market size for various types of potentially valuable carbon products derived from methane cracking using data from [78]. It is crucial to remember that carbon product cost can vary greatly depending on carbon characteristics and purity. Applying methane cracking in novel molten media reactors with solar energy or plasma integration could represent promising ways for CO<sub>2</sub> free hydrogen production taking the advantages of different pyrolysis processes (Figure 5(a) and

(b)). Presently, the separation and purification of high-value carbon products from catalysts are commonly achieved through acid treatment [84], despite its evident environmental disadvantages. Exploring alternative catalysts, such as perovskite-type materials, for methane pyrolysis offers a potential solution. This approach presents the advantage of generating metal oxide-carbon composite materials that can be directly utilized in energy-storage applications, such as batteries and solid oxide cells (SOCs), without the need for additional separation processes [85,86]. This direct utilization is illustrated in Figure 5(c). By employing these novel catalysts, the potential for mitigating environmental concerns and streamlining the production of valuable carbon products is evident. New materials and process design are also critical for the development novel technology separate the value carbon products and “regenerate” the metal-based catalysts.

#### **4.2. Engineering challenges and opportunities towards industrialization of methane pyrolysis**

Moving from laboratory-scale experiments to commercial-scale production poses a significant engineering hurdle. Ensuring that the process is both scalable and cost-effective at a larger scale necessitates meticulous engineering and optimization efforts. Several notable engineering obstacles must be tackled to achieve successful commercial deployment. High-temperature methane pyrolysis presents considerable technical complexities, underscoring the critical importance of achieving efficient heat transfer. It is imperative that heat is transferred to the reactor efficiently to initiate and sustain the pyrolysis reactions. Designing a reactor system capable of withstanding these extreme conditions while ensuring the efficient delivery of heat represents a major challenge. The use of a fluidized-bed reactor, which allows for the continuous addition and withdrawal of catalyst particles, is pivotal for industrial operation. Additionally, the dynamic movement of these particles facilitates efficient heat and mass transfer between the gas and the solid catalysts. Another promising reactor concept, particularly from an industrial perspective, is the moving-bed reactor, which has been developed by various partners in a funded collaborative project (Germany)[87]. In the moving-bed reactor, methane is introduced from the bottom of the reactor, while carbon catalysts are added from the top section. The solid carbon generated through methane pyrolysis accumulates on the carbon catalysts and is consistently eliminated from the bottom of the reactor. The moving-bed reactor offers significant advantages. This type of reactor enables excellent heat transfer between the gas and the solid catalyst without back-mixing, providing precise control over residence time for both phases [88]. The counterflow operation allows for energy integration within the reactor, while the outstanding heat transfer between the gas and solid particles ensures a thermally

efficient process. However, despite the potential for efficient heat transfer in these advanced reactor designs, managing the produced solid carbon remains a formidable process engineering challenge. This solid carbon tends to accumulate on the reactor walls over time, eventually leading to reactor clogging.

In recent years, there has been a growing interest in the utilization of liquid bubble column reactors employing molten metals, molten salts, molten metal alloys, or their combinations as both heat transfer and reaction media [14,21]. This approach is gaining prominence due to its distinct advantage of enabling the continuous separation of carbon products from the molten media, unlike traditional solid catalyst configurations. This feature greatly simplifies the management of carbon products and helps prevent reactor clogging, as solid carbon is consistently removed from the molten medium. It is important to note that while this technology holds significant promise, it is currently limited to laboratory-scale experiments. Addressing certain critical design parameters will be pivotal in its development. Specifically, minimizing the loss of molten metals or salts due to evaporation and devising effective containment strategies within the reactor are key considerations that need attention in the coming years. Additionally, reactors filled with molten metals or molten salts must be engineered to withstand the highly corrosive environment at high temperatures.

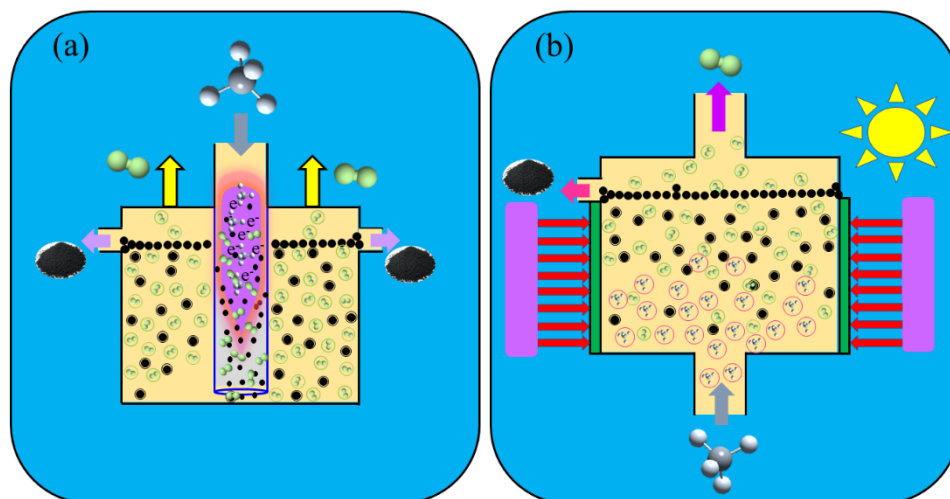
The reactor employed in methane pyrolysis should possess the ability to endure extreme conditions, including high temperature and pressure [14,15,17]. These conditions can result in material degradation and corrosion. Consequently, a significant engineering challenge lies in the development of reactor materials and designs that can effectively withstand these harsh conditions while ensuring long-term reliability. Efficient heat recovery is paramount to enhance energy efficiency and reduce operating costs. Engineers must, therefore, concentrate their efforts on creating streamlined heat recovery systems that can recover and reuse the heat generated during the process seamlessly integrated into the overall process design. Effectively managing carbon removal, storage, or utilization presents a central challenge in this context. Given that various methane pyrolysis processes for hydrogen production have own advantages and drawbacks, a viable strategy should combine the best features of different pyrolysis processes. By leveraging the strengths of various pyrolysis methods, it becomes realistic to develop cost-effective and energy-efficient processes primed for commercialization.

In the pursuit of overcoming these engineering challenges and advancing methane pyrolysis toward industrialization, interdisciplinary collaboration is indispensable. Chemists, materials scientists, mechanical engineers, and process engineers must work collaboratively to synergize

their expertise. Research and development endeavors aimed at enhancing efficiency, reliability, and cost-effectiveness in methane pyrolysis are paramount for its successful deployment in commercial settings. This, in turn, could play a significant role in nearing a more sustainable energy future.

#### 4.3. De-carbonization-connecting industry sectors

Methane pyrolysis has the potential to connect many industrial sectors, such as the iron and steel industry and direct carbon fuel cell with CO<sub>2</sub> capture, in order to reduce the carbon footprint of the related processes [89,90]. Although many challenges remain, CO<sub>2</sub> free hydrogen production via methane cracking is an attractive technology that has yet to realize its full commercial potential. The use of existing commercial natural gas network is the most appealing aspect for organizations involved in the energy business, demonstrating a significant economic advantage. Large corporations such as BASF and Monolith Materials are currently showing an increasing interest in methane cracking as a promising tool for producing hydrogen, which will hasten the commercialization of the methan



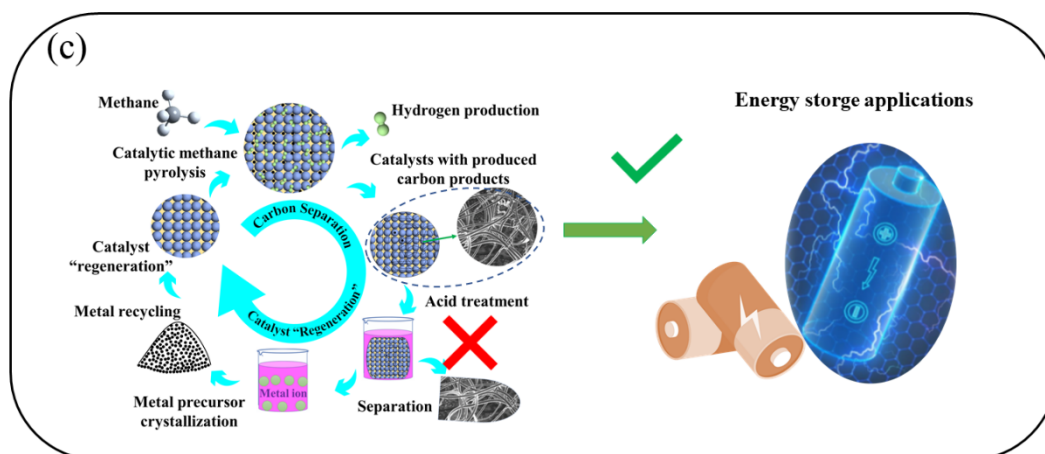


Figure 5. Schematic diagram on integrating novel molten media reactors with plasma (a) and solar energy (b) for methane cracking and (c) Illustration of metal oxide-carbon composite materials generated from thermal catalytic methane pyrolysis for energy-storage applications.

## 5. Concluding remarks

The benefits of transitioning to a hydrogen economy are commonly accepted and actively pursued. Clean hydrogen production is critical to achieving a low-carbon-emissions hydrogen economy. Methane pyrolysis emerges as one of the most promising routes for producing affordable and CO<sub>2</sub>-free hydrogen, in keeping with the urgent timetable required for climate action. Based on the goal for low-carbon hydrogen production, a thermal non-catalytic or plasma pyrolysis process for methane cracking appears to be the two of the highest potential approaches since they eliminate the need for purification and separation steps for pure H<sub>2</sub> production. The sale of the carbon products for potential applications will further lead to a significantly lower H<sub>2</sub> production cost. The development of in-situ characterization techniques, in conjunction with computational simulations and modeling, will greatly improve our understanding of methane cracking mechanisms, allowing for more efficient engineering approaches and material design for low-cost and CO<sub>2</sub>-free H<sub>2</sub> production. Further research in catalysis, finding new applications and uses of the produced carbon, improved CH<sub>4</sub> conversion and reactor design can make the methane cracking process competitive with SMR. Substantial efforts are still required to integrate the benefits of various pyrolysis processes and design the next-generation catalysts to meet the requirements under industrial conditions. Despite the long road ahead to commercial maturity, methane cracking currently holds one of the most promising

routes for near-term CO<sub>2</sub>-free hydrogen production on a large scale to keep up with the urgent climate action using existing natural gas infrastructure.

### **Competing interests**

The authors declare no competing interests.

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### **Authorship contribution statement**

**Guoxing Chen:** Conceptualization, Methodology, Validation, Funding acquisition, Writing – original draft. **Xiao Yu:** Methodology, Validation, Writing – review & editing. **Kostya (Ken) Ostrikov:** Methodology, Validation, Writing – review & editing. **Bowen Liu:** Writing – review & editing. **Jonathan Harding:** Writing – review & editing. **Gert Homm:** Funding acquisition, Writing – review & editing. **Heng Guo:** Validation, Writing – review & editing. **Stephan Andreas Schunk:** Writing – review & editing. **Ying Zhou:** Funding acquisition, Supervision, Writing – review & editing. **Xin Tu:** Funding acquisition, Supervision, Writing – review & editing. **Anke Weidenkaff:** Funding acquisition, Supervision, Writing – review & editing.

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