

State of the Art of Hydrogen Production via Pyrolysis of Natural Gas

Stefan Schneider^{[1],*}, Siegfried Bajohr^[1], Frank Graf^[1,2], Thomas Kolb^[1,2]

Abstract

Fossil fuels have to be substituted by climate neutral fuels to contribute to CO₂ reduction in the future energy system. Pyrolysis of natural gas is a well-known technical process applied for production of, e. g., carbon black. In the future it might contribute to carbon dioxide-free hydrogen production. Production of hydrogen from natural gas pyrolysis has thus gained interest in

research and energy technology in the near past. If the carbon by-product of this process can be used for material production or can be sequestered, the produced hydrogen has a low carbon footprint. This article reviews literature on the state of the art of methane / natural gas pyrolysis process developments and attempts to assess the technology readiness level (TRL).

Keywords: Hydrogen, Methane pyrolysis, Natural gas pyrolysis, Technology readiness level

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1 Introduction

Due to their large energy storage and transport capacities, the gas infrastructure in Germany and Europe can make a significant contribution to the successful implementation of the energy turnaround. In order to achieve the CO₂ emission reduction targets, fossil natural gas will have to be increasingly substituted by climate-neutral gases in the medium term. In addition to gases from renewable sources such as biogas from fermentation or gasification of biomass and hydrogen or methane (SNG) from PtG processes, the provision of hydrogen via reforming or pyrolysis of natural gas is currently being discussed. In the case of the latter two options, the carbon contained in the natural gas molecules ends as CO₂ or solid carbon. In order to achieve a positive effect in terms of greenhouse gas emissions, the carbon containing product formed must be permanently removed from the global carbon cycle or be used for material production. While steam reforming of natural gas for hydrogen production is state of the art, especially in the chemical and petrochemical industry, pyrolysis of natural gas for hydrogen production has not yet been commercialized in large scale. This paper reports on the state of the art of natural gas pyrolysis processes and research approaches reported in literature. It attempts to assess the technology readiness level (TRL) of the different processes reported.

2 Fundamentals of Methane Pyrolysis

Methane pyrolysis is the thermal decomposition of methane. Using nickel as catalyst, methane conversion in the percentage

range is observed above approx. 500 °C [1]. Without a suitable catalyst, the decomposition reaction starts at temperatures above 700 °C [2]. In order to achieve technically relevant reaction rates and methane conversion rates, the temperature must be considerably higher, i.e., for catalytic processes above 800 °C, for thermal processes above 1000 °C, and when using plasma torches at up to 2000 °C [3].

The main reaction of methane pyrolysis is endothermic and ideally produces solid carbon and gaseous hydrogen according to the following reaction equation:



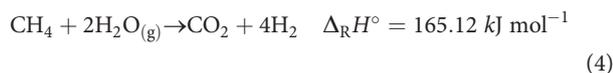
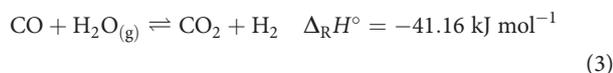
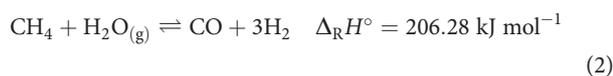
In most literature sources, the pyrolysis of methane is discussed as a synonym for the pyrolysis of natural gas for large-scale hydrogen production without CO₂ emissions [3, 4]. Methane pyrolysis is always evaluated in comparison to steam reforming, as this is the state of the art for the production of

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hydrogen from natural gas. Steam reforming of natural gas is an endothermic process that requires temperatures of 750 °C to 900 °C and pressure above 30 bar on a Ni-based catalysts [5]. Steam reforming can be described by the following Eqs. (2)–(4):



From a material point of view, Eq. (1) shows that methane pyrolysis produces two molecules of hydrogen and one molecule of carbon from one methane molecule. In steam reforming, Eq. (4), the conversion of water vapor releases twice the amount of hydrogen, but also one CO₂ molecule.

Energetically, the reaction enthalpy for hydrogen production by methane pyrolysis ($\Delta_{\text{R}}H^\circ = 37 \text{ kJ mol}^{-1} \text{ H}_2$) corresponds approximately to that of steam reforming ($\Delta_{\text{R}}H^\circ = 41 \text{ kJ mol}^{-1} \text{ H}_2$) if the energy for providing the water vapor is not taken into account. If the evaporation of the water ($\Delta_{\text{vap}}H^\circ = 44 \text{ kJ mol}^{-1} \text{ H}_2\text{O}$) is considered, in total $\Delta_{\text{R}}H^\circ = 63 \text{ kJ mol}^{-1} \text{ H}_2$ must be applied for steam reforming, which means that the process is energetically less favorable than the pyrolysis process. However, it should be noted that all pyrolysis processes described in literature are operated under near atmospheric pressure conditions at the current stage of development, whereas steam reforming is operated at higher pressure.

In all cases, the process-specific heat loss and the expenditure for hydrogen compression required must be taken into account for assessment of the energy efficiency. Furthermore, it should be noted that Eq. (1) of the methane pyrolysis describes only the main reaction path. In addition to the actual target products hydrogen and carbon, side reactions produce further saturated and unsaturated hydrocarbons and (poly)cyclic aromatic compounds, which can occur in all three states of aggregation [6–8]. If technically pure hydrogen has to be produced, e.g., as feedstock for the chemical or petrochemical industry, the product gas of methane pyrolysis must therefore be further conditioned by appropriate gas purification. If hydrogen is used as a chemical fuel, a significantly lower purity of the hydrogen is required and, thus, the conditioning requires much less effort.

In technical processes, natural gas and not methane is used as feed stock; therefore, when evaluating the technology readiness levels of the various processes described in literature, a distinction must be made between methane and natural gas pyrolysis. Theoretical considerations and laboratory experiments are usually carried out with methane without taking into account other reaction partners. In addition to methane, however, real natural gases usually contain a large number of other compounds (CO₂, H₂O, higher hydrocarbons, sulfur compounds, etc.) [9], which also react under pyrolysis conditions and thus have a significant influence on selectivity, products,

and conversion rate. Experimental and theoretical results on methane pyrolysis can therefore only be transferred to natural gas to a limited extent. This applies in particular to the product gas quality, the catalyst service life, and the solid deposits in the reactor.

As shown in Eq. (1), the pyrolysis of methane theoretically produces one mole of carbon and two moles of hydrogen per mole of methane. A simple balance of mass and energy (calorific value-related) yields the following values:

$$\text{Mass : } 1 \text{ t CH}_4 \rightarrow 250 \text{ kg H}_2 + 750 \text{ kg C} \quad (5)$$

$$\text{Energy : } 50000 \text{ MJ} + \Delta_{\text{R}}H^\circ \rightarrow 30000 \text{ MJ} + 24600 \text{ MJ} \quad (6)$$

From the point of view of the mass balance, carbon is the main product of methane pyrolysis and should be used as process product to increase the economics of a process. Such utilization must be CO₂-neutral if the hydrogen produced by the pyrolysis process is to be assessed as being CO₂-neutral. Depending on the pyrolysis process, the carbon product, often also referred to as thermal black or carbon black, is characterized as large primary particles of high density and purity and can be a valuable industrial product [10]. Its use as a substitute for coal or crude oil products is also being discussed [11] but is not relevant with regard to the avoidance of CO₂ emissions in hydrogen production. If carbon sequestration is desired, solid carbon from methane pyrolysis is advantageous over gaseous CO₂ from steam reforming, as the solid could be deposited, e.g., in former coal mines. From an energetic point of view, the calorific value of the product gas is reduced to approx. 60 % compared to the natural gas due to the removal of solid carbon.

On a large scale, natural gas pyrolysis was first used around 1930 in the thermal black process [12]. This process, which is still employed sporadically today, serves to produce high-quality carbon black products. The yield of solid carbon is approx. 40 %; the resulting hydrogen and gaseous by-products are used as fuel to heat the discontinuously operated reactors. In the last decades, the thermal black process has been increasingly replaced by the furnace black process. The feedstocks are usually inferior refinery by-products. By varying the relevant operating parameters, this process allows the production of nearly all carbon black grades [13].

Due to the efforts to reduce CO₂ emissions from the conversion and use of fossil fuels, the production of hydrogen increasingly comes into focus. Assuming the availability of cheap natural gas, pyrolysis processes have the potential to produce hydrogen at a moderate price and with a low CO₂ footprint, if the reaction enthalpy required for pyrolysis can be provided without CO₂. In 2016, Machhammer et al. estimated product costs of 2600 to 3200 € t⁻¹ of hydrogen (depending on projected revenues for the by-product carbon), which have to be compared to 2000 € t⁻¹ of hydrogen from steam reforming [4]. The technical challenges in all natural gas pyrolysis processes are the high conversion rates required for the economic operation of a process and the associated high process temperatures, the product gas purity, and the handling of solids generated from the gas phase, which can lead to deposits or even blockings.

3 Methane Pyrolysis Process Overview

The methane pyrolysis processes described in literature can be divided into three categories (Fig. 1). For the thermal decomposition of methane, reaction temperatures of well over 1000 °C are required [1]. If the process heat is provided via the reactor walls, soot deposits on hot surfaces, which typically leads to operational disturbances and a deterioration in heat transfer [14].

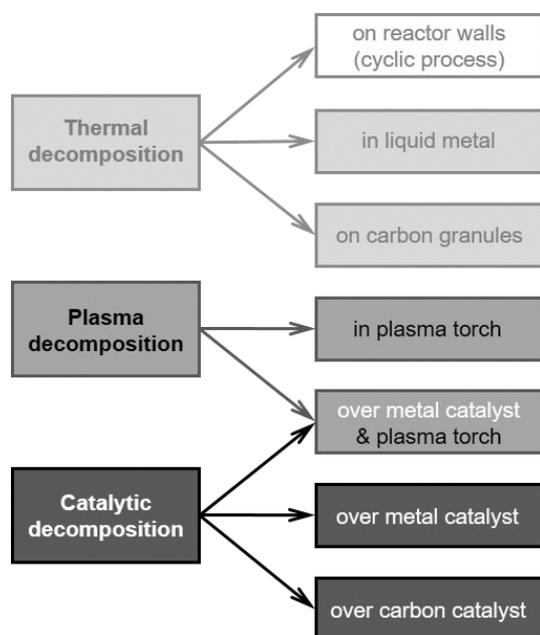


Figure 1. Categories of methane pyrolysis processes.

In plasma decomposition, high local energy densities and temperatures of up to 2000 °C are generated by means of a plasma torch. Large gas volume flows are usually recirculated to stabilize the plasma. In the area of the actual plasma torch, cooling, electrode wear, and carbon deposits are among the greatest technical challenges.

The catalytic decomposition of methane typically shows satisfying reaction rates and conversion rates already at temperatures well below 1000 °C. However, the active catalyst surface is usually deactivated after a short time by the solid carbon formed on it. Mechanical destruction of the support is reported caused by the incorporation of carbon in the catalyst.

Tab. 1 gives an overview of the pyrolysis processes described below, classified according to the three categories mentioned above. Only those processes are presented that have achieved at least a technology readiness level of TRL3 [15]. Numerous proof-of-principle studies on methane pyrolysis, particularly with regard to the reaction kinetics and other possible catalysts, can be found in [8, 16–18].

3.1 Thermal Decomposition

A thermal pyrolysis process for natural gas was developed by a consortium around BASF SE as part of a research project of the German Federal Ministry of Education and Research [11, 19–21]. The primary goal of the process is the production of hydrogen, however, the carbon product is intended to be used commercially. In a moving-bed reactor, carbon granules are conducted in counterflow to the gas phase at temperatures of up to 1400 °C (Fig. 2). The cold gas flow is preheated by the hot granules leaving the reactor. In the reaction zone, the carbon bed is directly heated by electrodes. It is postulated that the pyrolysis reaction takes place mainly at the surface of the granules. This assumption is supported by the observed growth of the carbon granule particles passing through the reactor. The hot product gas leaving the reactor finally heats the cold carbon granules entering the reactor. Depending on the desired hydrogen quality, treatment of the product gas by pressure swing adsorption (PSA) is suggested. The authors point out that cooling the product gas for heat recovery may also lead to by-product condensation. The scale-up of the process is being developed in an ongoing research project [22].

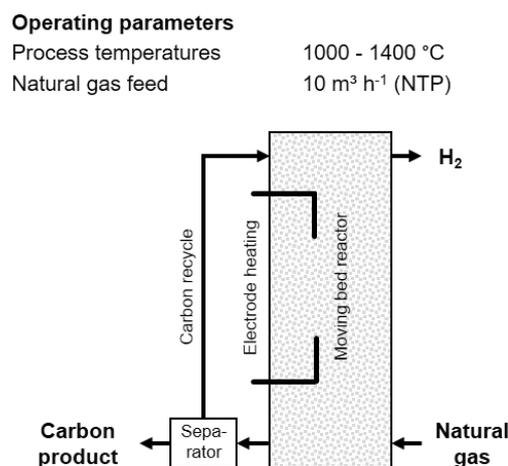


Figure 2. Operating parameters and schematic of the directly electrically heated moving-bed reactor according to [11, 23].

Together with the Institute for Advanced Sustainability Studies e. V. (IASS), a research group at the Karlsruhe Institute of Technology (KIT) developed a process for methane pyrolysis in liquid metal to produce hydrogen [24–27]. In this process, methane is thermally decomposed at temperatures of up to 1200 °C when passing through a liquid tin filled bubble column reactor (Fig. 3). In previous test campaigns, it was found that a small amount of carbon was deposited on the heated wall (approx. 10 µm layer thickness after several days of operation). Ideally, most of the produced solid carbon floats as powder on the liquid tin and may be separated. The laboratory reactor is operated with a methane volume flow up to 0.012 m³h⁻¹ (NTP). The process is not completely represented with the experimental set-up, as there is no continuous soot separation and tests so far can only be performed in batch operation with regard to the tin inventory. A scaling is not yet foreseeable [28];

Table 1. Overview of methane/natural gas pyrolysis processes.

Principle	Developer, facility	Target product	Period	Reactor description	State of development	TRL
Thermal	BASF	H ₂	2012–	Moving bed of carbon granules	Laboratory plant, R&D project for scale-up	4
Thermal	KIT / IASS	H ₂	2013–	Liquid tin bubble column	Laboratory, R&D project for process development	3
Plasma	Kvaerner	Carbon black	1992–2003	Plasma torch	Pilot plant, with subsequent scale-up (Karbomont plant)	6
Plasma	Kvaerner, Karbomont plant	Carbon black	1997–2003	Plasma torch	Production plant (decommissioned and dismantled)	8
Plasma	Monolith materials, Seaport plant	Carbon black	2014–2018	Plasma torch (similar to Kvaerner)	Pilot plant (dismantled), with subsequent scale-up	6
Plasma	Monolith materials, Olive Creek Plant	Carbon black	2016–	Plasma torch (similar to Kvaerner)	Production plant, mechanical completion planned for 2020	8
Plasma	Atlantic hydrogen, carbonsaver	Mixture H ₂ / natural gas	2005–2015	Plasma torch	Pilot plant (not put into operation), development stopped due to bankruptcy	5
Catalytic / Plasma	Tomsk Universities, TOMSK-GAZPROM	H ₂	2008–	Microwave, Ni catalyst bed + plasma torch	Laboratory, no further information on scale-up	3
Catalytic	UOP, HYPRO process	H ₂	1963	2-stage fluidized bed with Ni catalyst	Laboratory plant, development was stopped	4
Catalytic	Florida Solar Energy Center	H ₂	2003–2005	2-stage fluidized bed with C catalyst	Laboratory, no information on further development	3
Catalytic	Hazer Group	H ₂	2010–	3-stage fluidized bed with Fe catalyst	Laboratory, pilot plant to be constructed by 2021	3

however, two research projects have been started for further process development [29].

Operating parameters

Process temperatures	750 - 1175 °C
Methane feed	0.012 m ³ h ⁻¹ (NTP)
Methane conversion	78 %
Reactor space	1,6 l

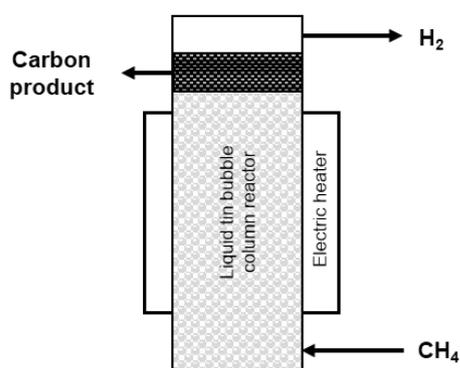


Figure 3. Operating parameters and schematic of the laboratory reactor at KIT according to [28].

3.2 Plasma Decomposition

In the 1990s, the Norwegian company Kvaerner patented a plasma torch for the production of carbon black through pyrolysis of natural gas and higher hydrocarbons [30–33]. In this process, natural gas is fed to a plasma torch which is operated with recirculated hydrogen and electric power. After successful operation of a pilot plant with a plasma output of 3 MW, the Karbomont plant with an annual thermal black production of 20 000 t was set up in Canada in 1997 [34]. The plant was decommissioned and dismantled in 2003; one of the reasons cited was the insufficient quality of the thermal black [35].

In 2012, the US company Monolith Materials started the development of a plasma process (Fig. 4) based on the Kvaerner technology and the work by Fulcheri et al. at MINES ParisTech with carbon black as primary target product [36, 37]. The operation of a pilot plant (Seaport Plant) was successful, but the plant was dismantled in 2018, no reasons given [38]. In parallel to this project, construction of the Olive Creek plant in Nebraska started in 2016 with a scheduled carbon black production of 10–15 kt a⁻¹. Commissioning was planned for 2018 [3]. However, according to the current status, the plant will not be mechanically completed before 2020 [39]. The produced hydrogen will be torched in the first stage of completion. Later

Operating parameters Seaport-plant

Temperature reaction zone	2100 °C
Natural gas feed	144 m ³ h ⁻¹ (NTP)
Methane conversion	94 %
Plasma power (electr.)	0.85 MW

Operating parameters Olive-Creek-plant (under construction)

Carbon black output	10 - 15 kt a ⁻¹
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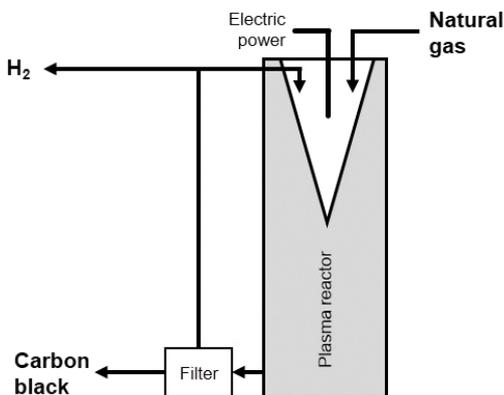


Figure 4. Operating parameters and schematic of the monolith process according to [40, 41].

on, the hydrogen is planned to be used for energy production in a nearby power plant [40].

The Canadian company Atlantic Hydrogen has developed a process where natural gas is decomposed in a plasma torch (Fig. 5). The original aim was to enrich natural gas with hydrogen before distribution in the gas grid [42, 43]. The prototype with a feed gas flow of 50 m³h⁻¹ (NTP) demonstrated the complete process, and the plant was used in an industrial environment. In test campaigns, natural gas was enriched with up to

Operating parameters Carbonsaver-plant

Process temperature	800 °C
Natural gas feed	50 m ³ h ⁻¹ (NTP)
Methane conversion	35 %
Plasma power (electr.)	5 kW

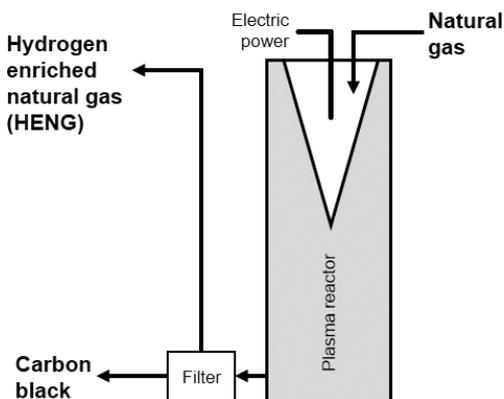


Figure 5. Operating parameters and schematic of the Atlantic Hydrogen pilot plant according to [42].

20 % hydrogen. Furthermore, up to 4 % higher hydrocarbons in the product gas were reported. During the construction of a larger pilot plant near the Irving Refinery in Canada in 2015, the company went bankrupt, the technology was not followed up [44, 45].

In 2008, the universities in Tomsk, Siberia, in cooperation with the company TOMSK-GAZPROM, patented a process (Fig. 6) that combines a plasma torch with a catalyst stage (Fig. 6) that combines a plasma torch with a catalyst stage [46–48]. The process is described to be based on effects induced by microwave radiation. In the pyrolysis reactor, a metallic catalyst bed is heated by microwaves and, according to the authors, micro-discharges occur between the catalyst particles, which support the decomposition of the natural gas. The further reaction finally takes place in a downstream plasma torch positioned at the end of the catalyst bed [49–51]. No approach on scaling up the laboratory apparatus has been published so far. An experimental setup where natural gas is exclusively split in a plasma torch without the use of catalysts was last described in 2018 [52].

Operating parameters

Process temperature	1000 °C
Natural gas feed	1 m ³ h ⁻¹ (NTP)
Methane conversion	80 % (Ni catalyst)
Microwave power (electr.)	1.5 kW

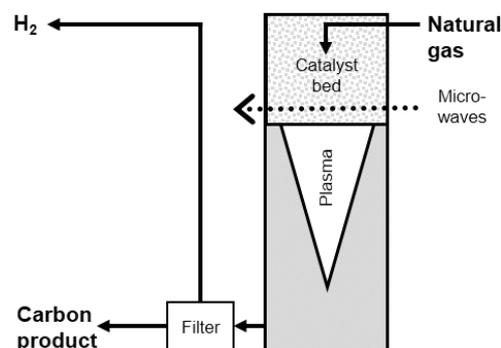


Figure 6. Operating parameters and schematic of the laboratory facilities in Tomsk according to [47, 49].

3.3 Catalytic Decomposition

In the 1960s, the HYPRO process was developed by the company Universal Oil Products (UOP) [53] with the aim of providing hydrogen for refinery processes. In this process, light hydrocarbons are decomposed in a fluidized bed over a nickel catalyst at 800–1100 °C. The catalyst is continuously regenerated in a second fluidized bed by burning the resulting carbon black. This method is similar to the FCC process for cracking liquid hydrocarbons in refineries. Due to the complexity and cost of the catalyst solids circulation, this process could not prevail over the well-established steam reforming process. Furthermore, in the HYPRO process, the converted carbon is released as CO₂ from the combustion stage, which excludes its use for the low-CO₂ production of hydrogen if CO₂ is not used or sequestered. So far, one laboratory plant with a methane throughput of up to 7 m³h⁻¹ was built in

Illinois (USA). The development of the method was not continued [54].

A research project presented by the Florida Solar Energy Center in 2003 is based on the catalytic effect of carbon particles on the pyrolysis of natural gas with hydrogen as the target product [55]. Similar to HYPRO, the process proposed and patented in this project by Muradov et al. [56, 57] is based on two separate fluidized bed reactors: a pyrolysis reactor and another reactor where heat is provided, and the carbon catalyst is being regenerated. As shown in Fig. 7, some of the PSA-separated off-gases are partially oxidized with air. It is postulated that the resulting water vapor and CO₂ activate the catalyst by partial gasification. The throughputs of the laboratory apparatus described are below 0.3 m³ h⁻¹ (NTP). The complete process is not tested, as there is no continuous catalyst regeneration. The latest publication dates from 2005 [56], there is no indication that this development was continued.

Operating parameters

Process temperature	900 °C
Natural gas feed	0.3 m ³ h ⁻¹ (NTP)
Methane conversion	60 %
Catalyst	Carbon

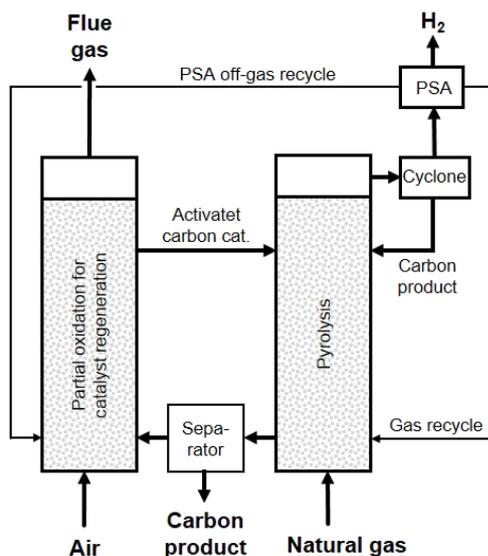


Figure 7. Schematic of the process proposed by Muradov et al. according to [56], and operating parameters of the laboratory facilities [55].

In 2016, the Australian company Hazer patented a fluidized-bed process where natural gas is to be decomposed to produce hydrogen using catalytically active iron ore (Fe₂O₃/Fe₃O₄) [58–60]. According to the patent description, the hydrogen yield, the product quality of the pyrolysis carbon, and the deactivation of the catalyst material can be controlled by pressure, temperature, and mass flow in the reactor. The three-stage countercurrent fluidized-bed system with different pressure stages shown in Fig. 8 was implemented on a laboratory scale. The described methane flow of 0.01 L min⁻¹ is very low. According to press releases, the laboratory facility has been

Operating parameters

Process temperature	850 °C
Methane feed	0.01 l min ⁻¹ (NTP)
Methane conversion	92 %
Catalyst	Fe ₂ O ₃ / Fe ₃ O ₄

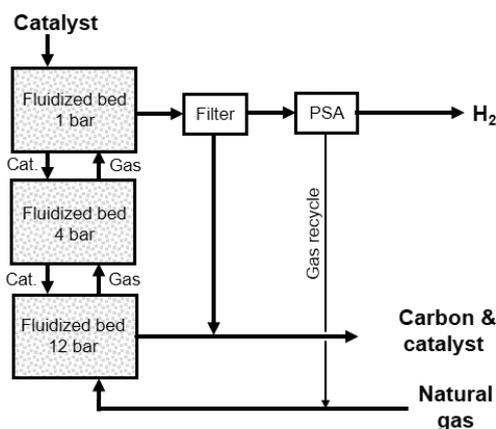


Figure 8. Operating parameters and schematic of the Hazer process according to [58].

expanded in terms of throughput; construction of a pilot plant is planned for 2021 [61–64].

4 Summary

Steam reforming of natural gas is a state-of-the-art process for hydrogen production. Pyrolysis of natural gas has not yet been commercialized under the aspect of hydrogen production. This paper reports on the development of natural gas pyrolysis processes and research approaches described in literature and attempts to assess their technology readiness level (TRL).

The process concepts for methane pyrolysis can be divided into three categories: (i) thermal decomposition, (ii) plasma decomposition, and (iii) catalytic decomposition. The process overview (see Tab. 1) shows that plasma processes for the production of carbon black from natural gas have been realized on industrial scale (e.g., Kvaerner process, KARBOMONT plant, TRL 8) and are still being further developed (Olive Creek plant, mechanical completion planned 2020, TRL 8). In these processes, hydrogen is used as a by-product to produce thermal energy. After successful operation of a pilot plant (Carbonsaver process, TRL 5), a plasma torch for the production of hydrogen-enriching natural gas was not developed further. Process approaches on thermal decomposition (KIT process, TRL 3), catalyst/plasma decomposition (TOMSK-GAZPROM consortium, TRL 3), and catalytic decomposition (e.g., Hazer Group, TRL 3) are still at a very early stage of development. Only BASF's thermal process (carbon granules in a moving bed, TRL 4) is already being further developed for scale-up.

Literature is often limited to the pyrolysis of methane as a single molecule and the challenges arising from the use of natural gas are not addressed. The quality of the produced hydrogen product gas is only sporadically reported. The quality and the use of carbon, which are important for the economic effi-

ciency of the process, are typically not addressed in a reliable manner.

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Frank Graf studied Process Engineering at the University of Karlsruhe and Economics at FernUniversität Hagen and received his doctorate from the Engler-Bunte-Institute in 2007. He heads the division Gas Technology of the DVGW Research Center at Engler-Bunte-Institute and is responsible for the research area “Physico-Chemical Fuel Processing” at the Engler-Bunte-Institut – Fuel Technology. His main research topics are the generation and processing of gases from renewable sources.



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Symbols used

$\Delta_{\text{R}}H^{\circ}$	[kJ mol ⁻¹]	reaction enthalpy under standard conditions
$\Delta_{\text{vap}}H^{\circ}$	[kJ mol ⁻¹]	enthalpy of evaporation under standard conditions

Abbreviations

FCC	fluid catalytic cracking
NTP	normal temperature and pressure
PSA	pressure swing adsorption
PtG	power-to-gas
SNG	substitute natural gas
TRL	Technology Readiness Level

References

- [1] N. Muradov, *Int. J. Hydrogen Energy* **2005**, *30* (3), 225–237. DOI: <https://doi.org/10.1016/j.ijhydene.2004.03.033>
- [2] M. Steinberg, *Int. J. Hydrogen Energy* **1999**, *24* (8), 771–777. DOI: [https://doi.org/10.1016/S0360-3199\(98\)00128-1](https://doi.org/10.1016/S0360-3199(98)00128-1)
- [3] R. A. Dagle, V. Dagle, M. D. Bearden, J. D. Holladay, T. R. Krause, S. Ahmed, *An Overview of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products*, U.S. Department of Energy, Washington, DC **2017**. DOI: <https://doi.org/10.2172/1411934>
- [4] O. Machhammer, A. Bode, W. Hormuth, *Chem. Eng. Technol.* **2016**, *39* (6), 1185–1193. DOI: <https://doi.org/10.1002/ceat.201600023>
- [5] H. Hiller, R. Reimert, H.-M. Stönner, *Gas Production, 1. Introduction*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim **2011**. DOI: https://doi.org/10.1002/14356007.a12_169.pub3

- [6] B. L. Crynes, W. H. Corcoran, L. F. Albright, *Pyrolysis, theory and industrial practice: Theory and industrial practice*, Academic Press, New York **1983**.
- [7] C. Guéret, M. Daroux, F. Billaud, *Chem. Eng. Sci.* **1997**, *52* (5), 815–827. DOI: [https://doi.org/10.1016/S0009-2509\(96\)00444-7](https://doi.org/10.1016/S0009-2509(96)00444-7)
- [8] G. Fau, N. Gascoin, P. Gillard, J. Steelant, *J. Anal. Appl. Pyrolysis* **2013**, *104*, 1–9. DOI: <https://doi.org/10.1016/j.jaap.2013.04.006>
- [9] G. Hammer, T. Lübcke, R. Kettner, M. R. Pillarella, H. Recknagel, A. Commichau, H.-J. Neumann, B. Paczynska-Lahme, *Natural Gas*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim **2011**. DOI: https://doi.org/10.1002/14356007.a17_073.pub2
- [10] W. Klose, *Terminology for the description of carbon as a solid*, Vol. 3, Kassel University Press, Kassel **2009**.
- [11] A. Bode, C. Anderlohr, J. Bernnat, F. Flick, F. Glenk, D. Klingler, G. Kolios, F. Scheiff, A. Wechsung, M. Hensmann, S. Möhring, G. Stubbe, C. Lizandara, A. Lange de Oliveira, S. Schunk, V. Göke, J. Hunfeld, D. Mihailowitsch, S. Pleintinger, H. Posselt, M. C. Weikl, H.-J. Zander, N. Antweiler, K. Büker, M. Eckbauer, M. Krüger, P. Marek, K. Rosermund, U. Janhsen, H. Mittelstädt, C. Möllers, D. W. Agar, A. Munera-Parra, *Solids and fluid products from gas-FfPaG*, final report BMBF FKZ 033RC1301 A-G, Bundesministerium für Bildung und Forschung, Bonn **2018**.
- [12] M. Voll, P. Kleinschmit, *Carbon*, *6. Carbon Black*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim **2010**.
- [13] E. M. Dannenberg, *J. Polym. Sci., Part B: Polym. Lett.* **1977**, *15* (10), 631–632. DOI: <https://doi.org/10.1002/pol.1977.130151013>
- [14] A. Abánades, E. Ruiz, E. M. Ferruelo, F. Hernández, A. Cabanillas, J. M. Martínez-Val, J. A. Rubio, C. López, R. Gavela, G. Barrera, C. Rubbia, D. Salmieri, E. Rodilla, D. Gutiérrez, *Int. J. Hydrogen Energy* **2011**, *36* (20), 12877–12886. DOI: <https://doi.org/10.1016/j.ijhydene.2011.07.081>
- [15] *HORIZON 2020 WORK PROGRAMMES 2016- 2017, 20th General Annexes*, European Commission, Brussels **2017**.
- [16] U. P. M. Ashik, W. M. A. Wan Daud, J.-I. Hayashi, *Renewable and Sustainable Energy Rev.* **2017**, *76*, 743–767. DOI: <https://doi.org/10.1016/j.rser.2017.03.088>
- [17] H. F. Abbas, W. M. A. Wan Daud, *Int. J. Hydrogen Energy* **2010**, *35* (3), 1160–1190. DOI: <https://doi.org/10.1016/j.ijhydene.2009.11.036>
- [18] N. Muradov, *Int. J. Hydrogen Energy* **2017**, *42* (20), 14058–14088. DOI: <https://doi.org/10.1016/j.ijhydene.2017.04.101>
- [19] H.-J. Maaß et al., *Patent WO2013/004398 A3*, **2013**.
- [20] H.-J. Maaß et al., *Patent EP2729404 B1*, **2018**.
- [21] H.-J. Maaß et al., *Patent US9359200 B2*, **2016**.
- [22] A. Bode, *New process for clean hydrogen*, BASF Research Press Conference, Ludwigshafen, Januar **2019**.
- [23] J. Kellenbenz, D. Klingler, A. Bode, *Methane pyrolysis – Innovative process for the coupled production of hydrogen and carbon*, Annual meeting of the ProcessNet High Temperature Technology Group, Frankfurt am Main, January **2017**.
- [24] T. Geißler, M. Plevan, A. Abánades, A. Heinzl, K. Mehravar, R. K. Rathnam, C. Rubbia, D. Salmieri, L. Stoppel, S. Stückrad, A. Weisenburger, H. Wenninger, T. Wetzel, *Int. J. Hydrogen Energy* **2015**, *40* (41), 14134–14146. DOI: <https://doi.org/10.1016/j.ijhydene.2015.08.102>
- [25] T. Geißler, A. Abánades, A. Heinzl, K. Mehravar, G. Müller, R. K. Rathnam, C. Rubbia, D. Salmieri, L. Stoppel, S. Stückrad, A. Weisenburger, H. Wenninger, T. Wetzel, *Chem. Eng. J. (Amsterdam, Neth.)* **2016**, *299*, 192–200. DOI: <https://doi.org/10.1016/y.cej.2016.04.066>
- [26] A. Abánades, T. G. Geißler, T. Wetzel, *Patent EP3521241 A1*, **2019**.
- [27] A. Abánades, T. G. Geißler, T. Wetzel, *Patent WO2019/154732 A1*, **2019**.
- [28] T. Geißler, *Methane pyrolysis in a liquid metal bubble column reactor*, Dissertation, Karlsruhe Institute of Technology (KIT), **2017**.
- [29] www.kit.edu/kit/pi_2019_wasserstoff-aus-erdgas-ohne-co2-emissionen.php (Accessed on April 22, 2020)
- [30] B. Gaudernack, S. Lynum, *Int. J. Hydrogen Energy* **1998**, *23* (12), 1087–1093. DOI: [https://doi.org/10.1016/S0360-3199\(98\)00004-4](https://doi.org/10.1016/S0360-3199(98)00004-4)
- [31] S. Lynum et al., *Patent WO93/20153*, **1993**.
- [32] S. Lynum et al., *Patent US6068827*, **2000**.
- [33] S. Lynum et al., *Patent EP0616599*, **1996**.
- [34] J. A. Bakken, R. Jensen, B. Monsen, O. Raanes, A. N. Wærnes, *Pure Appl. Chem.* **1998**, *70* (6), 1223–1228. DOI: <https://doi.org/10.1351/pac199870061223>
- [35] M. Gautier, V. Rohani, L. Fulcheri, *Int. J. Hydrogen Energy* **2017**, *42* (47), 28140–28156. DOI: <https://doi.org/10.1016/j.ijhydene.2017.09.021>
- [36] N. J. Hardman, *Reinf. Plast. (London)* **2017**, *61* (3), 145–148. DOI: <https://doi.org/10.1016/j.repl.2017.02.002>
- [37] N. J. Hardman, *US Patent 2017 0073522 A1*, **2017**.
- [38] www.monolithmaterials.com/pilot-plant (Accessed on April 22, 2020).
- [39] www.monolithmaterials.com/olive-creek/project-update-details (Accessed on June 19, 2020).
- [40] R. Hanson, Special Use Permit Application For Construction And Operation Of A Carbon Black Manufacturing Plant By Monolith Nebraska, LLC, Village of Hallam, NE **2018**. www.lincoln.ne.gov/cnty/clerk/agenda/2018sm/180927/hallamextraterritorialzoning%20.pdf
- [41] N. J. Hardman et al., *Patent WO2017048621 A1*, **2017**.
- [42] T. Boutot, J. Bullerwell, Z. Liu, W. Niu, T. K. Whidden, Y. Yang, *ECS Trans.* **2009**, *16* (50), 155. DOI: <https://doi.org/10.1149/1.3157945>
- [43] T. Boutot et al., *Patent WO2007019664 A1*, **2017**.
- [44] www.cheminst.ca/magazine/article/its-a-heat-wave 2014 (Accessed on April 22, 2020).
- [45] www.businesswire.com/news/home/20150929006065/en/Atlantic-Hydrogen-Files-Bankruptcy (Accessed on April 22, 2020).
- [46] Y. D. Korolev, O. B. Frants, N. V. Landl, V. G. Geyman, A. G. Zerlitsyn, V. P. Shiyan, Y. V. Medvedev, *IEEE Trans. Plasma Sci.* **2009**, *37* (12), 2298–2302. DOI: <https://doi.org/10.1109/TPS.2009.2032546>
- [47] S. I. Galanov, A. G. Zherlitsyn, Y. V. Medvedev, O. I. Sidорова, V. P. Shiyan, *Russ. J. Appl. Chem.* **2011**, *84* (6), 997–1002. DOI: <https://doi.org/10.1134/S1070427211060176>

- [48] A. G. Zherlitsyn, V. P. Shiyan, P. V. Demchenko, *Resour. Office. Technol.* **2016**, *2* (1), 11–14. DOI: <https://doi.org/10.1016/j.reffit.2016.04.001>
- [49] J. V. Medvedev et al., *Patent RU2317943 C2*, **2006**.
- [50] A. G. Zherlitsyn et al., *Patent RU2393988 C1*, **2006**.
- [51] A. G. Zherlitsyn et al., *Patent RU2522636 C1*, **2014**.
- [52] J. V. Medvedev, A. G. Levashkin, D. V. Sorochan, *Carbon And Hydrogen Production Technology From Natural Gas*, Tomsk State University, **2018**.
- [53] J. B. Pohlenz, N. H. Scott, *Patent US3284161*, **1966**.
- [54] A. Abánades, C. Rubbia, D. Salmieri, *Int. J. Hydrogen Energy* **2013**, *38* (20), 8491–8496. DOI: <https://doi.org/10.1016/j.ijhydene.2012.08.138>
- [55] N. Z. Muradov, *Thermocatalytic CO₂-Free Production of Hydrogen from Hydrocarbon Fuels*, Technical Report, No. DE-FC36-99GO10456, U.S. Department of Energy, Oak Ridge, TN **2004**. DOI: <https://doi.org/10.2172/828215>
- [56] N. Z. Muradov, *Int. J. Hydrogen Energy* **2005**, *30* (10), 1149–1158. DOI: <https://doi.org/10.1016/j.ijhydene.2005.04.005>
- [57] N. Z. Muradov, *US Patent 8 002 854 B2*, **2011**.
- [58] A. Cornejo, H. T. Chua, *Patent US2018/0065850 A1*, **2018**.
- [59] A. Cornejo, *Patent AU2016312962 B2*, **2016**.
- [60] A. Cornejo, *Patent WO2018/170543 A1*, **2018**.
- [61] www.smallcaps.com.au/pre-pilot-testing-improvements-hazer-groups-clean-process (Accessed on April 22, 2020).
- [62] www.thewest.com.au/business/hazer-plots-cracking-hydrogen-revolution-in-kwinana-ng-b88958562z (Accessed April 22, 2020).
- [63] www.soundtelegraph.com.au/?news%2Fsound-southern-telegraph%2Fkwinana-move-a-big-step-for-hazer-ng-b881136994zbclid=IwAR2bQlf9ZR_t0udyutn8QCPJP9agUYWaQv7rBwk06xYgNSk4OkMkI8fMZM (Accessed on April 22, 2020).
- [64] Hazer Group Limited, *Appendix 4C–31 December 2019, Company Update & Quarterly Cashflow Report*, Perth, WA **2019**. www.hazergroup.com.au/wp/wp-content/uploads/2020/01/200131-Appendix-4C-Quarterly-Cashflow-for-31-Dec-2019-FINAL.pdf

The paper provides a literature review on the status of worldwide research and development work on the production of hydrogen from the pyrolysis of natural gas, including an assessment of technological maturity (TRL).

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