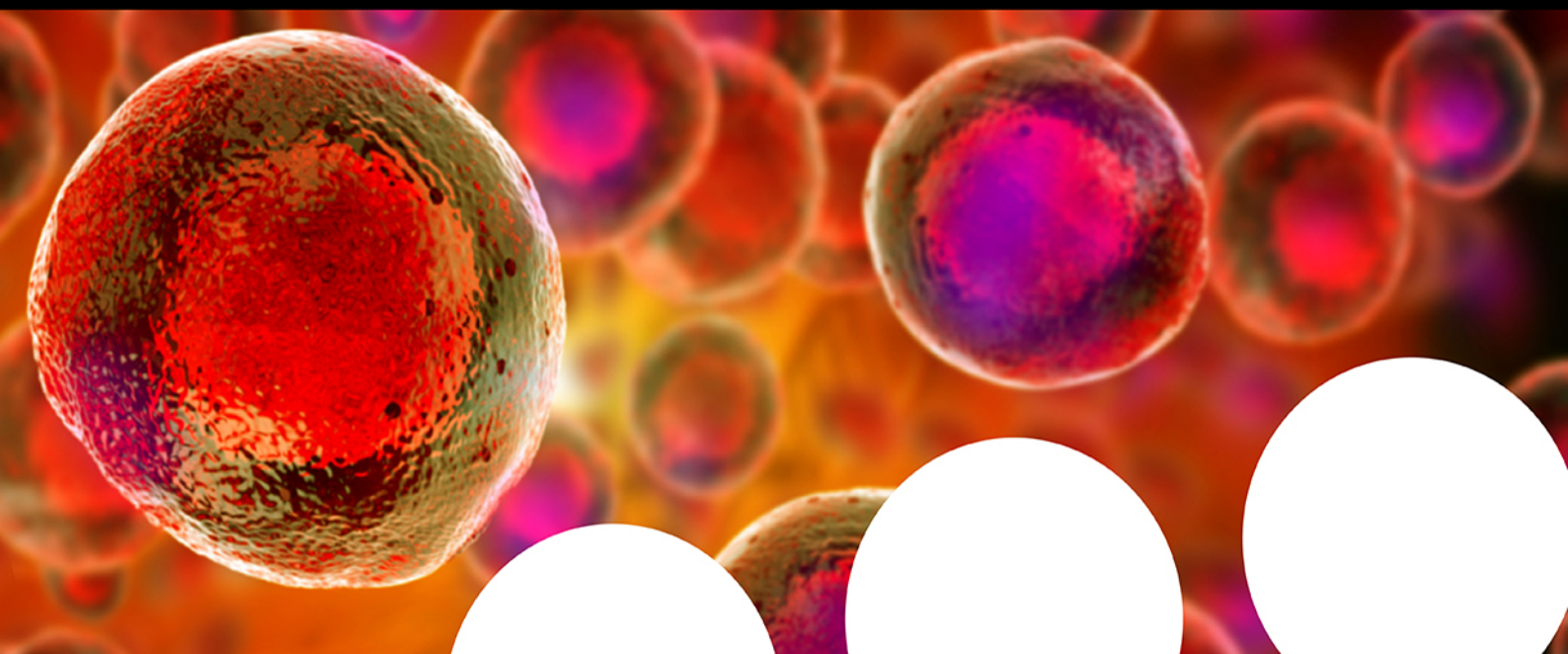


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Hydrogen Production and Carbon Capture by Gas-Phase Methane Pyrolysis: A Feasibility Study

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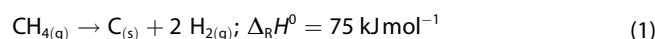
Using natural gas and sustainable biogas as feed, high-temperature pyrolysis represents a potential technology for large-scale hydrogen production and simultaneous carbon capture. Further utilization of solid carbon accruing during the process (i.e., in battery industry or for metallurgy) increases the process's economic chances. This study demonstrated the feasibility of gas-phase methane pyrolysis for hydrogen production and carbon capture in an electrically heated high-temperature reactor operated between 1200 and 1600 °C under industrially

relevant conditions. While hydrogen addition controlled methane conversion and suppressed the formation of undesired byproducts, an increasing residence time decreased the amount of byproducts and benefited high hydrogen yields. A temperature of 1400 °C ensured almost full methane conversion, moderate byproduct formation, and high hydrogen yield. A reaction flow analysis of the gas-phase kinetics revealed acetylene, ethylene, and benzene as the main intermediate products and precursors of carbon formation.

Introduction

With a demand of approximately 70 million metric tons in 2018, hydrogen (H₂) is already today a resource of tremendous importance that is predominantly used for refining processes and ammonia production.^[1] In the global strive for decarbonization, hydrogen is considered a key energy carrier for a future carbon-free energy economy,^[2] which will multiply the global need for hydrogen. Hydrogen's enormous potential for solving environmental and energy issues recently initiated a discussion about the most appropriate production technology.^[3] Although water electrolysis using renewable energy from wind and solar represents the only entirely carbon-free pathway towards hydrogen, high investment costs and a number of technological hurdles currently oppose its widespread short-term and large-scale realization.^[4] Therefore, focus has been laid on alternative hydrogen production processes.^[5] Currently, steam reforming of fossil natural gas with its main component methane (CH₄) provides the major share of hydrogen, but also results in considerable carbon dioxide (CO₂) formation that substantially increases the carbon footprint of the process.^[6] In contrast, the direct decomposition of methane into gaseous hydrogen and

elemental solid carbon, better known as methane pyrolysis [Eq. (1)], allows interrupting the carbon cycle.^[7]



Since CO₂ is continuously bound in vegetation, an overall bio-chemical process using biogas originating from biomass gasification as feed gas even offers the possibility to extract CO₂ from the atmosphere, which ultimately accounts for negative emissions during the pyrolysis of hydrocarbons. Herewith, pyrolysis exhibits a unique feature that makes it a highly attractive alternative to other sustainable hydrogen production processes. Irrespective of whether the necessary energy for CH₄ pyrolysis is provided via an electrically heated furnace as heat or via a (thermal) plasma, the energy intensity of methane pyrolysis is much lower compared, for instance, to water electrolysis.^[8] Under consideration of the current scarcity of renewable energy that should preferably be used for sustainable hydrogen production, the attractiveness of the methane pyrolysis process increases even further. Beyond simple sequestration, a further usage of carbon (i.e., for metallurgy, battery production, or agriculture) substantially increases the economic attractiveness of methane pyrolysis.^[3a,9] With regard to financial and ecological considerations, large-scale hydrogen production via methane pyrolysis provides a reasonable tradeoff between carbon footprint and process costs and is therefore considered an auspicious approach in industrial research and development.^[3a,10] Although heterogeneous catalysts based on nickel or iron can decrease the heat needed for CH₄ decomposition,^[10] fast catalyst deactivation due to coking as well as potential metal contaminations of the potentially salable reaction product carbon make an entirely thermal pyrolysis process most desirable in the light of techno-economic aspects.

Hydrocarbon pyrolysis for chemical vapor deposition (CVD) is a well-known topic throughout the scientific community and

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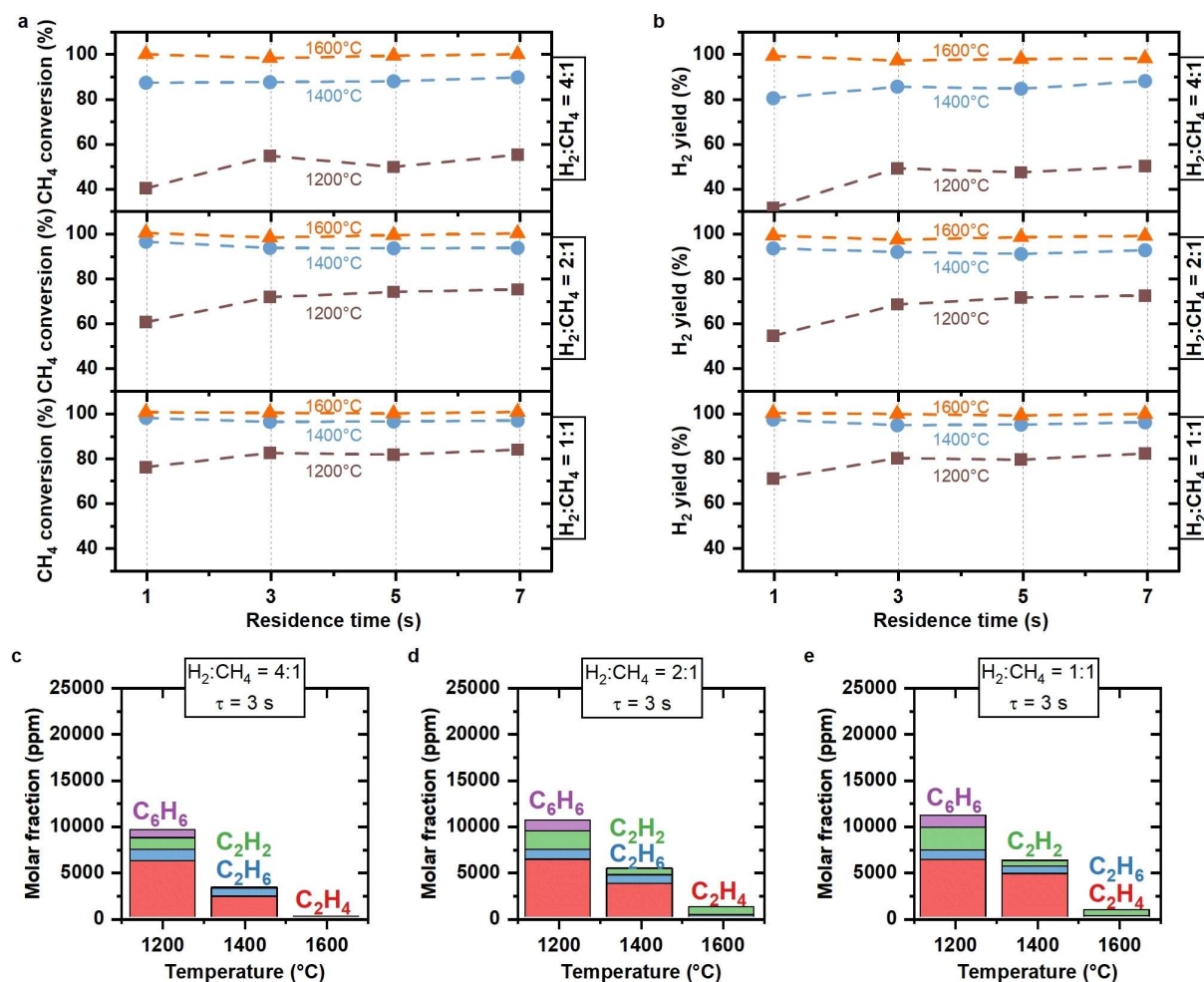


Figure 1. Impact of process parameters on methane conversion and byproduct formation. (a) Methane conversion vs. residence time at 1200, 1400, and 1600 °C for three different molar H₂/CH₄-ratios. (b) Hydrogen yield vs. residence time at 1200, 1400, and 1600 °C for three different molar H₂/CH₄-ratios. (c–e) Exemplary molar fractions of byproducts vs. temperature for different molar H₂/CH₄-ratios at a residence time of 3 s.

CVD from light hydrocarbons has been subject to numerous fundamental studies^[11] and several profound mechanistic investigations aimed at analyzing hydrocarbon decomposition and carbon deposition in detail.^[11b,12] Nevertheless, very recent publications in the context of pyrolysis and soot formation are still continuously adding new facets to the understanding of the interplay between homogeneous and heterogeneous reaction pathways during the complex multi-phase CVD process.^[13] By combining experiments conducted in an electrically heated high-temperature reactor and a numerical reaction flow analysis, our present study demonstrates the feasibility of gas-phase methane pyrolysis at high temperatures for producing gaseous hydrogen and capturing solid carbon under industrially relevant conditions. Hereby, we contribute to the global endeavor to develop sustainable technologies that reduce anthropogenic carbon emissions.



Figure 2. Solid carbon depositions as received after 60 min of reactor operation. Graphitic sheet-like carbon deposited on the reactor wall during methane pyrolysis and soot-like agglomerated carbon deposited at the reactor bottom. Conditions: 1400 °C; residence time 5 s; molar H₂/CH₄-ratio of 2:1.

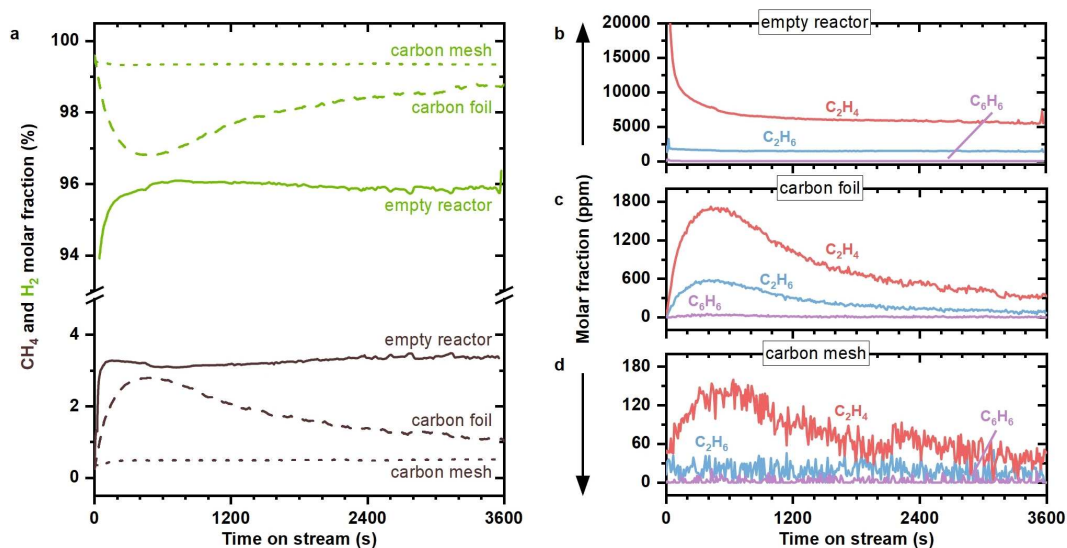


Figure 3. Impact of carbon on methane conversion. Molar fractions of product species vs. time on stream for an empty reactor and for reactor walls covered with carbon foil or carbon mesh. Conditions: 1400 °C; residence time 5 s; molar H₂/CH₄-ratio of 2:1. (a) Main species H₂ and CH₄. (b–d) Byproducts C₂H₄, C₂H₆, and C₆H₆.

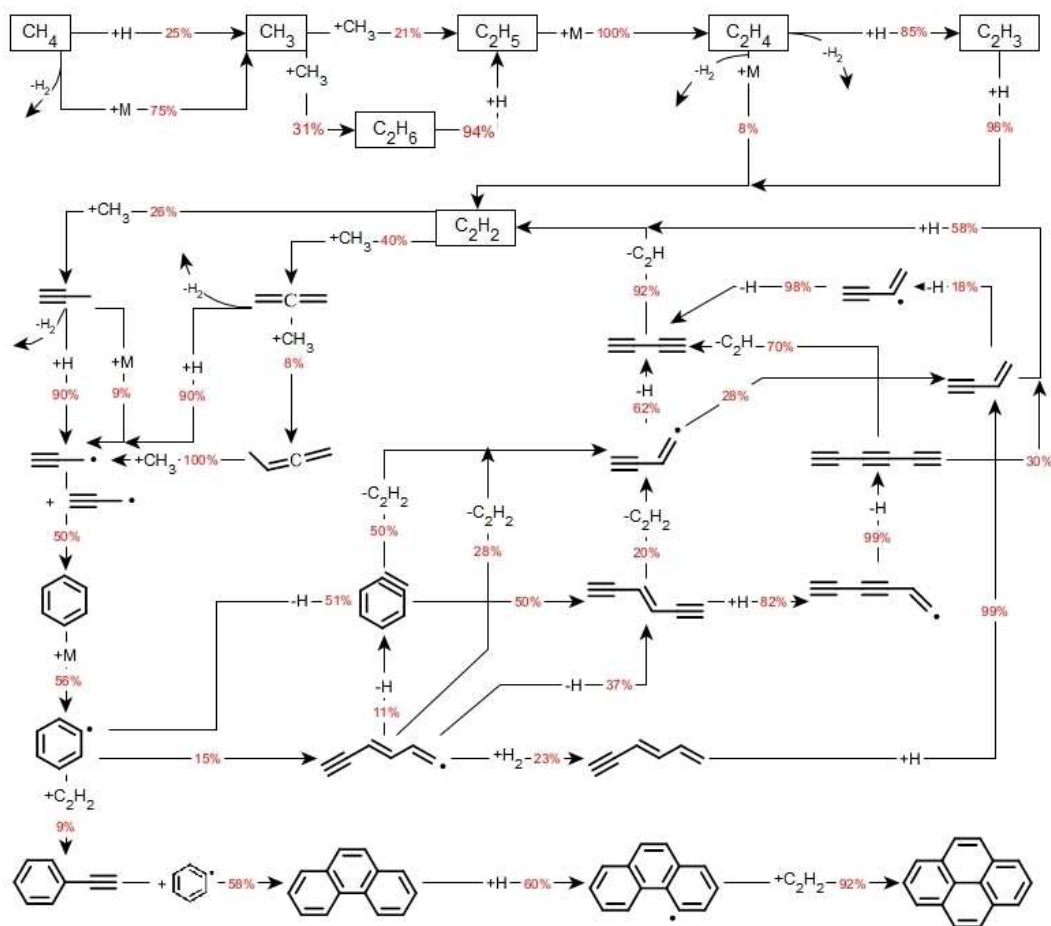


Figure 4. Mechanistic insights into methane pyrolysis. Integral reaction flow analysis for methane pyrolysis at 1400 °C; residence time 5 s; molar H₂/CH₄-ratio of 2:1.

Results and Discussion

An electrically heated ceramic α -Al₂O₃ reactor of 1.0 m length and a hot zone of 0.4 m length dedicated for investigating gas-phase chemistry at high temperatures, which has already been used in an earlier publication of our group^[14] and is described in detail in the Supporting Information, served as setup for our experimental measurement campaign. Mass flow controllers allowed for mixing a well-defined feed gas exclusively consisting of CH₄ and H₂ while an in-house developed LabView-based software tool monitored all relevant data like flow rates and the reactor temperature. Analyzing the effluent product gas stream with an on-line mass spectrometer provided information on the chemical processes taking place and uncovered the evolution of byproducts. By varying the H₂/CH₄-ratio, the residence time in the hot zone, and the reactor temperature, we investigated the influence of the most important process parameters on methane conversion and product selectivity at industrially relevant conditions. The addition of H₂ to the feed gas stream does not only allow controlling the reaction rate but also avoids clogging of the reactor.

At 1200 °C, a molar H₂/CH₄-ratio of 4:1 and a residence time of 1 s in the hot zone resulted in 40% CH₄ conversion (Figure 1a), with H₂ as main product (Figure 1b) and C₂H₂, C₂H₄, C₂H₆, and C₆H₆ as gaseous byproducts whose concentrations sum up to a total volumetric share of approximately 1.7%. A temperature increase to 1400 °C causes a pronounced increase of methane conversion to 87% and results in a moderate decrease of the byproduct concentrations (total volumetric share of \approx 1.1%) and an even further temperature rise to 1600 °C ultimately results in quasi-exclusive H₂ formation. Moreover, the data suggest that a declining H₂/CH₄ feed gas ratio favors high H₂ yields (Figure 1b), but also benefits the formation of byproducts as exemplarily illustrated for a residence time of 3 s in Figure 1c (byproduct data for other residence times showing analogous trends can be found in the Supporting Information). At 1400 °C and a residence time of 3 s, for instance, we found a H₂ yield of 87.6% and a total byproduct concentration of only 0.3% for a H₂/CH₄-ratio of 4:1, whereas 0.6% byproducts along with 95.5% H₂ yield were observed for a H₂/CH₄-ratio of 1:1. Hence, the H₂ content in the feed gas can be used to efficiently control methane conversion and byproduct formation in particular. These findings for homogeneous gas-phase methane pyrolysis are in analogy to recent studies in the context of catalytic^[15] and plasma-assisted^[16] non-oxidative coupling of methane to form value-added olefins, where the co-feeding of H₂ can increase the ethane and ethylene selectivity versus acetylene, for instance.^[16]

Mechanistic considerations suggest that this decrease of methane conversion in the presence of high H₂ levels is due to suppressed methyl radical formation, which is considered the rate-limiting step for the pyrolysis reaction.^[17] Although a higher contribution of the signal-to-noise ratio at low species concentrations makes the interpretation of the byproduct concentration trends more difficult, we can conclude that short residence times and low H₂ contents benefit the formation of undesired byproducts. Especially the decrease of the residence time from

3 to 1 s lowers the H₂ yield and goes along with a rising byproduct selectivity. Since product separation and purification is a decisive cost factor in industrial processes, a further decrease of the residence time is irrelevant in terms of real-world applications. In particular at short residence times, when a large amount of CH₄ enters the reactor, the assessment of the temporal evolution of the species concentrations reveals a slight increase of methane conversion with time on stream (see the Supporting Information). Since the reaction conditions remain unchanged, these slight changes point to an increasing contribution of heterogeneous deposition reactions^[18] favored by carbon that forms during the reaction. Although we also observed soot-like carbon deposits at the bottom of our reactor in the filter, the majority of carbon deposited as a graphitic sheet-like structure on the reactor walls (Figure 2).

With respect to the role of carbon, our findings confirm previous studies that investigated the beneficial effect of carbon on methane pyrolysis.^[19] Steady-state experiments with a H₂/CH₄-ratio of 2:1 and a residence time of 5 s at 1400 °C revealed that already a simple coating of the reactor walls with either a carbon foil or a carbon mesh, respectively, significantly enhances both the overall methane conversion and the selectivity towards H₂. While under these conditions approximately 4% of CH₄ were found in the outlet gas stream of the reactor without carbon-covered walls, the maximum CH₄ concentration was smaller than 3% for the experiment with carbon foil coated reactor walls (Figure 3a). In addition, the overall byproduct concentrations decreased substantially. The main byproduct ethylene, for instance, had a concentration of approximately 5550 ppm in the empty reactor, whereas its maximum concentration was less than 1800 ppm when the reactor wall was coated with a carbon foil (Figure 3b,c). A further increase of the carbon surface by replacing the carbon foil by a carbon mesh resulted in an even further decrease of the byproduct concentrations (Figure 3d) and nearly full methane conversion was achieved. Hence, the formation and presence of solid carbon results in an "autocatalytic" process that enhances the hydrogen yield. Note, that the transient features in the first minutes of each experiment will be subject to a subsequent upcoming mechanistic study. In the present study, particular focus is laid on the general trends that become clear when analyzing the time-on-stream data after the first 600 s, once the entire setup reached steady-state operation conditions and changes of the species concentration can be clearly attributed to the pyrolytic process and carbon deposition.

From a mechanistic point of view, the presence of carbon also accelerates heterogeneous deposition reactions.^[12a,c,19a,c] Carbon that is present in the reactor can act as a nucleus for further carbon deposition, which particularly explains the increasing methane conversion with time on stream observed throughout our experiments. On an atomic level, the high catalytic activity of carbon layers was attributed to a high defect concentration within the carbon structure, whereas highly ordered carbon was reported to show significantly less activity.^[20] In this respect, a larger carbon surface is beneficial, since a higher active surface area is available for the

reaction.^[11a,19a] Hence, carbon deposited during the reaction leads to an autocatalytic process accelerating the conversion rate. Consequently, the presence of carbon also affects by-product concentrations in the outlet gas stream and changes the deposition chemistry. Previously published results identified the ratio between the surface area A that is available for surface chemistry reactions and the reactor volume V (A/V -ratio) as a key driver for the equipoise between gas-phase and surface chemistry.^[11a,21] In this context, low A/V -ratios benefit gas-phase reactions that result in a fast transformation of C_2 species towards aromatic hydrocarbons, whereas surface chemistry and thus carbon deposition is favored for high A/V -ratios. Moreover, not only the decomposition chemistry but also the texture and morphology of pyrolytic carbon is strongly influenced by the process parameters.^[22]

The understanding of the complex product formation from gas-phase reactions is supported by an integral reaction flow analysis conducted with the DETCHEM software package^[23] (1D plug flow reactor model) and exemplarily shown in Figure 4 for a temperature of 1400 °C and a residence time of 5 s at a H_2/CH_4 -ratio of 2:1. A modified detailed gas-phase mechanism by Appel et al.^[24] allows to describe the pyrolytic C_1 and C_2 species, the formation of linear hydrocarbons till C_6 species, and the formation of benzene as well as further polyaromatic hydrocarbons (PAHs) up to pyrene. Based on this mechanism, Figure 4 illustrates the major reaction pathways, where the numbers (in red) represent the relative consumption and production rate, respectively, of the species in percent. The kinetic analysis identifies the initial formation of a methyl radical via the first H-atom abstraction as rate-determining step of methane pyrolysis. While the reaction flow analysis reveals ethane as a primary product at low residence time right after ignition, the formation of ethylene followed by sequential dehydrogenation to C_2H_2 becomes the dominant pathway of coupling to form longer chains at higher residence time and higher conversion rates. Under the conditions studied, the dimerization of propargyl radicals (C_3H_3) represents the main reaction toward the first aromatic ring, namely benzene (C_6H_6). Successive stages of H-abstraction and C_2H_2 -addition via the so-called HACA mechanism^[25] yield the PAHs ultimately culminating in the formation of pyrene ($C_{16}H_{10}$). In accordance with the experimentally observed gas-phase byproducts, the kinetic flow analysis identifies C_2H_6 , C_2H_4 , C_2H_2 , and C_6H_6 as the main products (Figure 4) and potential precursors of carbon deposition.

Conclusion

Our study demonstrates the feasibility of simple gas-phase methane pyrolysis for hydrogen production and carbon capture. The presented results contribute to understanding carbon deposition from methane at high temperatures and outline major parameters that are essential for maximizing hydrogen yields in the context of ecological and economic considerations. Although temperatures above 1400 °C ensure complete methane pyrolysis and minimize the formation of

byproducts such as ethylene or benzene to a negligible level, such extreme reaction conditions are not only demanding for the materials used in the setup but also consume significant amounts of energy. In contrast, temperatures below 1300 °C allow for reasonable methane conversion, however, at the cost of byproduct formation that necessitates a cumbersome and expensive purification of the product gas stream. In this context, variations of the residence time between 3 and 7 s only marginally bias the product composition, whereas the H_2/CH_4 -ratio constitutes a premier process parameter allowing for maximizing hydrogen selectivity and yield. From an industrial point of view, exclusive usage of H_2 and CH_4 as feed gas like demonstrated in our experiments drastically reduces the need for costly measures for separating the effluent product gas stream. Overall, the operational point of large-bore methane pyrolysis plants will be strongly driven by energy costs. Despite higher byproduct concentrations that require a gas purification of the effluent gas stream, the energetic considerations may favor operation at moderate temperatures between 1200 and 1300 °C. Herein, rational thermal management with suitable heat exchangers can contribute to reducing the overall energy consumption and the exclusive usage of green renewable power for heating maximizes the sustainability of the methane pyrolysis process.

Kinetic simulations and the integral reaction flow analysis suitably complement our experimental study to identify gaseous byproducts. The utilization of carbon that acts as a nucleus for further carbon deposition via a coagulation mechanism can promote methane pyrolysis and suppress byproduct formation. Our experiments demonstrate that a simple coating of the reactor walls with carbon substantially reduces byproduct formation and can ensure quasi-exclusive hydrogen formation. Moving fixed bed or fluidized bed reactors that have been previously discussed in academia and industry^[26] may be attractive solutions for realization of high-temperature methane conversion and carbon capture on an industrial large-bore level with higher gas velocity. Moreover, an overall bio-chemical process chain that relies on biogas as feed for the pyrolysis reaction offers the chance of an indirect capture and sequestration of CO_2 from the atmosphere. Since oxygen-containing species in biogas can significantly change the reaction network during methane pyrolysis, a profound kinetic analysis along with a comprehensive lab-scale measurement campaign that also comprises long-term reactor operation is an integral aspect for designing an industrially viable and robust process. Finally yet importantly, further usage of the formed solid carbon, for example, for metallurgy and batteries, can significantly increase the economic appeal of the overall process.^[3a,10]

Experimental Section

Experiments were conducted in a setup that can be operated at high temperatures of up to 1800 °C. After mixing the feed gas by means of mass flow controllers (Bronkhorst), the reaction gas mixture passed a non-porous ceramic $\alpha-Al_2O_3$ reactor (diameter $d=0.02$ m, length $l=1.0$ m; DEGUSSIT AL23 by Firatec/Aliaxis) that survives high-temperature experiments with reactive gases. Heating

elements and insulation created a hot zone of approximately 0.4 m length. The effluent gas stream was analyzed by an HPR-20 mass spectrometer (Hiden Analytical). For the integral reaction flow analysis that was performed with the DETCHEM^{PPR} code (DETCHEM software package^[23]), a reaction mechanism by Appel et al.^[24] was adapted and reduced to 247 reactions and 76 species that allowed describing the pyrolytic reaction pathways relevant in the context of methane pyrolysis. Further details on the experimental setup, data evaluation, and modeling are provided in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: carbon capture · decarbonization · gas-phase chemistry · hydrogen production · methane pyrolysis

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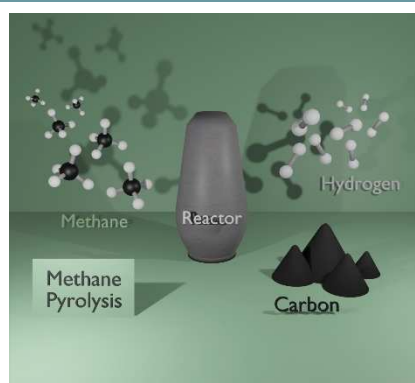
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RESEARCH ARTICLE

Methane pyrolysis: High-temperature pyrolysis of natural gas and sustainable biogas represents a potential technology for large-scale hydrogen production and simultaneous carbon capture. The study reports on gas-phase methane pyrolysis in an electrically heated high-temperature reactor operated between 1200 and 1600 °C. A systematic process operation parameter variation and a reaction flow analysis of the gas-phase kinetics provide guidance for process design.



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1 – 7

Hydrogen Production and Carbon Capture by Gas-Phase Methane Pyrolysis: A Feasibility Study

