

Contents lists available at ScienceDirect

International Journal of Hydrogen Energy

journal homepage: www.elsevier.com/locate/he



Optimizing methane plasma pyrolysis for instant hydrogen and high-quality carbon production

Oday Daghagheleh^{a,*}, Johannes Schenk^{a,b,**}, Heng Zheng^a, Michael Andreas Zarl^{a,b}, Manuel Farkas^b, Daniel Ernst^a, Lina Kieush^b, Markus Lehner^c, Nikolaos Kostoglou^d, Robert Obenaus-emler^e

^a Chair of Ferrous Metallurgy, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700, Leoben, Austria

^b K1-MET GmbH, Stahlstraße 14, 4020, Linz Austria

^c Chair of Process Technology and Environmental Protection, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria

^d Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Straβe 18, 8700, Leoben, Austria

e Resources Innovation Centre, Montanuniversität Leoben, Franz-Josef-Straβe 18, 8700, Leoben, Austria

ARTICLE INFO

Keywords: Natural gas pyrolysis Methane pyrolysis Hydrogen production Sustainability Green energy Thermal plasma Carbon Turquoise hydrogen

ABSTRACT

The European Green Deal has set a target for Europe to achieve net-zero greenhouse gas emissions by 2050, necessitating a transition to more sustainable energy sources. Hydrogen gas (H₂) has emerged as a promising solution, with methane pyrolysis presenting a viable method for its production. This study explores the optimization of methane plasma pyrolysis for hydrogen and high-quality carbon production. Employing a statistical approach by a design of experiment software, critical process parameters are systematically analyzed to predict their impact within a defined range. Additionally, the paper conducts comprehensive characterization of the solid carbon produced during pyrolysis using imaging, spectroscopic and elemental analysis, and gas sorption analysis methods. The experimental investigation was conducted using a thermal plasma reactor with several settings of influential parameters including methane gas (CH₄) content in the plasma gas, electric current, and arc length. The DC-transferred plasma arc is formed using a variable gas mixture of argon gas (Ar) and CH4, with a constant flow rate of 5 Nl/min. Thirteen tests were designed, evaluating responses such as power input, process stability, and H₂ yield. The H₂ yield indicates the hydrogen produced from CH₄, with 100% representing total conversion. While the process exhibited inconstancy, attributed to reactor design constraints, a high H₂ yield of 67%-100% was achieved. The results indicate that a higher CH₄ content in the plasma gas and extended arc lengths disturb the plasma arc, hence reducing the H2 yield. Increased power input, achieved through higher amperage levels, and a wider reaction zone eased by extending the arc length both led to an improved H₂ yield. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) revealed microstructural differences, with carbon samples from the filter exhibiting finer textures and carbon samples from the reactor larger sizes and dendritic particles. Raman spectroscopy confirmed crystalline graphitic-like structures with low defect concentrations, a finding supported by X-ray diffraction (XRD) analysis. Inductively coupled plasma mass spectroscopy (ICP-MS) analysis confirmed high-purity carbon with slight impurities from initial filter contamination. Brunauer-Emmett-Teller (BET) specific surface area calculations based on gas sorption analysis showed significant variations, with filter-collected samples exhibiting $40-170 \text{ m}^2/\text{g}$ and reactor-collected ones showing $7-30 \text{ m}^2/\text{g}$.

https://doi.org/10.1016/j.ijhydene.2024.07.129

Received 16 May 2024; Received in revised form 25 June 2024; Accepted 9 July 2024

Available online 14 July 2024

^{*} Corresponding author. Chair of Ferrous Metallurgy, Montanuniversität Leoben, Franz-Josef-Stra β e 18, 8700 Leoben, Austria.

^{**} Corresponding author. Chair of Ferrous Metallurgy, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria.

E-mail addresses: oday.daghagheleh@unileoben.ac.at (O. Daghagheleh), johannes.schenk@unileoben.ac.at (J. Schenk), heng.zheng@stud.unileoben.ac.at (H. Zheng), michael.zarl@k1-met.com (M.A. Zarl), manuel.farkas@k1-met.com (M. Farkas), daniel.ernst@unileoben.ac.at (D. Ernst), lina.kieush@k1-met.com

⁽L. Kieush), markus.lehner@unileoben.ac.at (M. Lehner), nikolaos.kostoglou@unileoben.ac.at (N. Kostoglou), emler@unileoben.ac.at (R. Obenaus-emler).

^{0360-3199/© 2024} The Author(s). Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

The European Green Deal, a set of policies approved by the European Commission, has set an ambitious goal for Europe - to achieve net-zero greenhouse gas emissions by 2050 [1]. As part of this initiative, the focus is on the transition from traditional fossil fuels to more sustainable and eco-friendly energy sources [2]. Hydrogen gas (H₂) has gained significant attention as a promising alternative energy carrier and a potential solution in this transition. Nevertheless, similar to other emerging technologies, the production, storage, and transportation of H₂ present several challenges [2,3]. The majority of H₂ utilized in industrial applications is currently derived from fossil fuels, primarily through conventional processes like steam methane reforming (SMR) [4-6]. Although electrolysis of water should ideally stand out as the only genuinely sustainable method for H₂ production, its widespread adoption as a primary source of H₂ faces challenges, primarily due to economic and energy-related constraints [3,6]. Considering the current infrastructure, in the immediate future, hydrocarbons are expected to continue serving as the primary H_2 feedstock [5,7]. Consequently, a method drawing interest is methane pyrolysis, a process that converts methane gas (CH_4) into H₂ gas and solid carbon, offering advantages worth considering [8-10]. The H₂ produced by this method is known as turquoise hydrogen, which acts as a bridging technology towards achieving completely carbon-free H₂ production [2,11]. Notably, in methane pyrolysis, carbon oxide is not released into the atmosphere; instead, carbon is deposited as solid carbon, readily available for utilization [10].

The demand for H₂ is rapidly increasing, according to the Net Zero Emissions by 2050 (NZE) scenario outlined by the International Energy Agency (IEA) [12,13]. Given that approximately 75% by weight of CH₄ is converted into solid carbon as a by-product, the methane pyrolysis process could potentially generate a considerable amount of high-value solid carbon. Hence, the characterization of the resulting carbon is pivotal in finding suitable applications and, subsequently, offsetting production costs [14].

Various methods have been proposed for methane pyrolysis, with plasma technology being one of the intriguing options [15–25]. Plasma offers advantages, as it can provide the necessary energy for the process and can be turned on and off without additional heating or processing steps [26]. This is particularly useful for on-site applications like hydrogen-based steelmaking since it allows for immediate adjustments in hydrogen supply, eliminating the need for long-term storage. Furthermore, thermal plasma normally operates at extremely high temperatures, up to 10000 K, eliminating the need for catalysts [27]. Certain plasma systems may even exceed this temperature range. This is significant because catalysts can be problematic due to carbon buildup and concerns about product purity. However, understanding plasma technology can be complex and relies on experiments additional to theoretical calculations.

Fincke et al. [28] investigated methane plasma pyrolysis using a direct current (DC) plasma reactor. They studied specifically the carbon yield with respect to the gas residence time and suggested a model for the carbon growth. They also studied other possible reaction products, such as acetylene (C_2H_2) and benzene (C_6H_6). Two measures to increase the carbon yield were offered: first, to increase the process pressure, thus the reactant concentration, and second, to increase the nucleation rate by providing nucleation sites, for instance, graphite electrodes.

Lee et al. [29] made use of a DC thermal plasma system with three torches. They focused on the CH₄ conversion rate and the resulting products, including H₂ and C₂H₂, by varying the CH₄ flow rate and quenching conditions. H₂ concentration in the product gas increased when CH₄ flow rate was increased, and the quenching rate was reduced. At the same time, a higher CH₄ flow rate reduced the CH₄ conversion rate. They also reported that produced carbon showed characterizations close to carbon black (CB), with a more graphitized structure. But they could not find a relation between the process parameters and the carbon

properties. Li et al. [30] used the same principle by a DC plasma setup. They studied the effect of different gas injection methods on the plasma stability and CH_4 conversion rate to H_2 and C_2H_2 . They declared that the conversion rate is higher when Ar and CH_4 are pre-mixed and introduced through the plasma torch, but the graphite electrode erosion is more severe. They also confirmed that increasing CH_4 in the gas mixture impacted the plasma stability and limited the testing time. In contrast to that, when CH_4 was introduced after the torch outlet, it did not influence the plasma state.

Boutot et al. [8] have used a patented plasma torch to partially convert natural gas to H_2 and solid carbon. They demonstrated that increased pressure necessitates higher voltages for operation, and pressure levels exceeding 2 bar would demand additional power supply, thereby increasing the cost of the process. They also investigated the produced carbon and reported it as a structured mixture of amorphous and nanostructured carbons. They addressed the issue of process stability and its limitations: The deposition of carbon on the surface of the electrodes can lead to bridging and short circuits, resulting in immediate interruptions of the plasma arc.

Maslani et al. [31] used a slightly different approach. They worked with a DC plasma torch, using water vapor and argon gas (Ar) as plasma gas stabilizers, while CH_4 was introduced to the reactor separately. They studied the CH_4 conversion rate and the system's energy balance by changing the CH_4 flow rate. They stated that a higher flow rate of CH_4 leads to a lower conversion rate. Additionally, they studied the formed carbon, which seems to be well-defined spherical particles of 1 μ m in size. However, carbon oxides were also found in the product gas due to the presence of water vapor in the system.

Kim et al. [32] also employed a DC plasma torch combined with a radio frequency (RF) torch for H₂ production. They focused on the characterization of the produced carbon using microstructure investigation methods. They reported that depending on the sample position in the reactor, the carbon showed slightly different structural properties. They also explained that samples from the chamber's inner wall have a more crystalline structure compared to the fine carbon collected in the product gas filter. Simply because the carbon from the reaction chamber is exposed to high temperatures for longer periods. In another study [33], they identified the produced carbon as nanostructured sheet-like carbon and studied it extensively. They concluded that the size of the product is influenced by the plasma temperature, which is regulated by the power input. At low power supply and temperature ranges, product formation is inhibited, resulting in the retention of small structures exhibiting a turbostratic arrangement akin to CB. At elevated temperatures, the reaction promotes carbon growth, resulting in the formation of 2-D sheet-like synthetic carbon. This thermal environment facilitates crystal growth, yielding sheet-like carbon structures characterized by a high specific surface area of up to 49 m^2/g and a significant degree of crystallization. Consequently, these properties render the material attractive for various applications, such as energy storage and fuel cells.

Fulcheri et al. [34] used a three-phase alternative current (AC) plasma connected individually to three graphite electrodes using H_2 -nitrogen gas (N_2) as plasma gas. CH_4 was introduced to the plasma zone from a separate inlet. They studied the CH_4 conversion rate and the carbon product and also attempted to define the system's energy balance. According to their calculation and comparison to an electrolysis process, their process has 25 kWh/kg of H_2 energy intensity, 42% of that for electrolysis, which is around 60 kWh/kg of H_2 . They observed that the carbon particles display an aggregate morphology similar to CB, although the primary nuclei do not exhibit the spherical or turbostratic characteristics typical of CB. This variation in characterization was attributed to the higher reactor temperature compared to conventional furnaces used for CB production. These findings are interpreted as promising indicators that such a product could potentially capture a significant share of the CB market.

This study explores the concept of H₂ production through methane pyrolysis, aiming to refine critical process parameters and to understand

their qualitative connections to specific outcomes. While previous studies have attempted to establish correlations between various factors and outcomes, not all have succeeded. This work uses a statistical approach via a design of experiment software to analyze these factors and predict their impact within a defined range. The aim is to simplify the discussion by conducting a systematic study focusing on selected process parameters and their effects. Another unique aspect is the indepth investigation of the solid carbon produced during pyrolysis. Various characterization techniques, including scanning electron microscopy (SEM) and combined with energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy, and X-ray diffraction (XRD), are employed for imaging and spectroscopic analysis. Furthermore, inductively coupled plasma mass spectroscopy (ICP-MS) is utilized for elemental analysis and to confirm the purity of the product. N2 adsorption and desorption measurements at 77 K were employed to estimate the specific surface area (SSA) of the produced carbons on the basis of the Brunauer-Emmet-Teller (BET) method.

2. Concept and methodology

The underlying concept involves subjecting CH_4 to the plasma arc, leading to its decomposition into H_2 and solid carbon. The H_2 should subsequently be collected and enriched while the carbon residue undergoes further processing for utilization as a valuable second product. Fig. 1 visually illustrates the demonstrated concept. Investigating and optimizing both H_2 production and carbon quality is vital.

An experimental investigation was conducted, designing a series of experiments using the MODDE® 13 Pro software from Sartorius AG to determine optimal conditions.

2.1. Experimental work

The tests were conducted using a thermal plasma facility located at the Chair of Ferrous Metallurgy at Montanuniversität Leoben, as depicted in Fig. 2. While this facility has been extensively utilized for steelmaking research [35–38], certain modifications were necessary for purposes of the current study. Notably, the reaction chamber was entirely constructed from graphite to prevent impurities. The function is explained in detail in a previous publication [39], therefore, here, it is only briefly explained.

The facility provides a DC-powered plasma arc in the range of 1–16 kVA. Manual control of current flow is achieved through a thyristor (also known as a silicon-controlled rectifier or SCR) integrated into the power unit. Both amperage and voltage are recorded during the experiments.

The plasma arc is vertically ignited between a graphite hollow



Fig. 1. Illustration of the study concept for hydrogen and carbon production using green electricity. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

cathode and a graphite anode pin within the graphite reaction chamber. In current experimental setup, CH_4 alone cannot act as the plasma gas; to stabilize and facilitate pyrolysis, a mixture of Ar and CH_4 is necessary. This is because Ar, being monoatomic, requires lower atomization and ionization energy, which enhances the plasma arc stabilization [39]. Additionally, using Ar as an inert gas is essential for mass balance calculations, as it remains constant and does not react. The next section explains the evaluation methods in detail. The total gas flow was maintained at a constant rate of 5 Nl/min.

Following the process, the resulting gas exits the reactor and undergoes dust removal using a ceramic hot gas filter. Subsequently, the product gas is analyzed by a gas mass spectrometer. A camera system integrated into the top lid of the furnace provides a live stream of the arc.

Flexibility to vary certain parameters that have a critical impact on the process allows to study the influence on the outcome. The selected influential parameters were CH₄ content in the plasma gas, electric current, and arc length, with corresponding responses being H_2 yield, power input, and stability time, listed in Table 1. Each of these responses is explained and discussed in corresponding subsections.

Thirteen tests (P1–P13) were performed, which included three dedicated to confirming experimental reproducibility. In addition to process parameters, comprehensive characterization of the produced carbon was performed, involving analyses to elucidate morphological, microstructural, elemental, and surface area properties. The results of the carbon characterization studies are reported in section 4.

Both H_2 yield and power input were calculated from the raw data, while the stability time, a steady process time without disruption, was recorded and documented during the test. The calculation equations and the evaluation method of the results will be undertaken in the subsequent section.

2.2. Evaluation

The mass spectrometer provides volume fractions for the specified gas components (Ar and H_2) recorded in cycles, each lasting 5–6 s. The gas analysis is applied for thermodynamic calculations of H_2 volume in the product gas. To calculate the absolute volume of H_2 in each cycle, the initial step involves computing the constant volume of Ar. This is achieved by multiplying the Ar flow rate per second by the cycle time in seconds, as indicated in Equation (1). Subsequently, Equation (2) is used to determine the H_2 volume in each cycle. The absolute volume of H_2 in the product gas is then computed, taking into account its ratio percentage to Ar, given that Ar is an inert gas and remains constant.

$$V_{Ar} = t_{cyc} \cdot V_{Ar}$$

$$V_{H_{2-produced}} = C_{V,H_2} \cdot \frac{V_{Ar}}{C_{V,Ar}}$$

Where $V_{H_2_produced}$, V_{Ar} denote the respective gas volume [NI] for each measuring cycle, and C_{V,H_2} and $C_{V,Ar}$ represent the respective gas concentration [vol. %] in the product gas during each cycle. \dot{V}_{Ar} stands for the volume flow rate of the input gas [Nl/min], and t_{cyc} indicates the time of a measuring cycle [min]. With a consistent CH₄ flow introduced to the reactor gas, the CH₄ inlet for each cycle can be calculated like that of Ar, according to Equation (3).

$$V_{CH_{4-in}} = t_{cyc} \cdot \dot{V}_{CH_{4-in}}$$

 $\dot{V}_{CH_{4-in}}$ represents the volume flow rate of CH₄ input, while $V_{CH_{4-in}}$ refers to the gas volume [NI] in the measuring cycle. Therefore, the H₂ yield can be calculated as the ratio of produced H₂ and the CH₄ inlet, using Equation (4).

$$H_2 yield = \frac{V_{H_2-produced}}{2 \cdot V_{CH_4-in}} \cdot 100$$



Fig. 2. Layout of the thermal plasma facility used in this study [39].

 Table 1

 The variable factors for the design of experiments and the resulting responses.

Test Name	Factors (pre-defined inputs)			Responses (the resulting changes)			
	CH4 [%]	Electric current [A]	Arc Length [mm]	H ₂ yield [%]	Power input [kW]	Stability time [s]	
P1	20	90	15	79	4.44	6.5	
P2	20	120	15	90	5.19	20.4	
Р3	20	105	15	76	4.26	30.0	
P4	40	90	15	79	4.97	4.8	
P5	40	120	15	99	6.50	5.6	
P6	20	90	25	100	5.19	13.2	
P7	20	120	25	94	3.98	15.4	
P8	40	90	25	68	5.46	2.3	
P9	40	120	25	70	7.77	1.8	
P10	30	105	20	90	6.00	4.7	
P11	30	105	20	83	5.86	2.6	
P12	30	105	20	96	5.07	5.8	
P13	30	105	20	96	5.20	3.2	

The power input cannot be directly adjusted, however, the amperage is controlled through the thyristor. Employing Equation (5), the power input is calculated based on data obtained from the transformer.

$$Power input [kW] = \frac{I \cdot V}{1000}$$
5

Where I represents the current in amperes, and V represents the voltage in volts.

2.3. Example for test interpretation

To make it easier to understand the data analysis of the pyrolysis test, it is helpful to show an example of the data observed during the test and the subsequent interpretation. For instance, Fig. 3 illustrates three distinct stages encountered during a pyrolysis test. The initial stage involves purging, where only Ar is introduced to eliminate other gases and air from the reactor. The actual pyrolysis experiment begins when the arc is ignited with a contact and short circuit of the electrodes, as depicted in Fig. 3. Immediately, the arc length is extended to 10 mm to avoid overheating of the electric supply unit and forming a stable plasma arc. The thyristor level is pre-set in the 95–100% range for the initial plasma arc supported only by Ar. Subsequently, the gas is switched to the intended Ar and CH₄ mixture, and the thyristor level is adjusted to achieve the desired amperage. Consequently, a brief peak in power can



Fig. 3. Examples of product gas and power input analysis during a pyrolysis test.

be observed in the initial seconds, labelled as 1 and 3 for phases 1 and 2, respectively. Peak 2 represents a failed attempt to initiate the arc.

It is noteworthy that immediately after the onset of the pyrolysis phases, there is a gradual increase in H_2 in the product gas. However, based on experiments, there is a delay until H_2 is detected by the gas mass spectrometer. This delay is termed as the H_2 response time, which is consistently defined as 4 min for subsequent evaluations on the basis of initial measurements, as shown in Fig. 4.

The observed drop in power is attributed to a momentary deviation of the plasma arc, denoted as 4 and 5 in Fig. 3, almost disrupting the arc. The worst scenario is total arc disruption, indicated by label 6.

The H_2 yield rates and the power input during pyrolysis were calculated, as illustrated in Fig. 4. The H_2 response time delineated on the H_2 yield curve served as the reference point for data extraction in the design of experiments. Consequently, the H_2 yield value after the 4-min response time is considered the response value. The 4-min H_2 response time was chosen as it signifies the point at which the curves stabilize and reach a continuous state.



Fig. 4. An example for H₂ yield and power input rate of the pyrolysis test.

2.4. Materials and characterization

The solid carbon generated from methane pyrolysis can exhibit diverse morphologies, ranging from amorphous carbon to structured graphitic materials and even nanostructures such as carbon nanotubes and fibers [40]. The value and quality of this solid carbon are pivotal determinants of its market price. Consequently, obtaining a high-quality carbon product holds the potential to enhance revenue streams and expedite the return on investment period for large-scale pyrolysis plants [41].

Existing literature highlights the influence of several key parameters, notably reactor geometry, operating temperature, and plasma gas flow rate, on the characteristics of the produced carbon [8,42]. In the study from Boutot et al. [8], it was determined that the reproducibility of the carbon varied significantly, making it challenging to establish a clear link between the varying conditions and the resulting carbon properties [8,42]. Nevertheless, it was noted that the characteristics of the samples depended on their source, whether they were collected from the gas filter or directly from the reactor itself [8].

In this study, the produced carbon underwent detailed characterization using various analytical techniques to elucidate its nature and quality.

2.4.1. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

SEM is a technique that creates magnified images that reveal microscopic and even nanoscopic-scale information on a specimen's size, shape, composition, and other properties. Characterization of the samples was performed using a JEOL 7200 F field emission SEM (JEOL Germany GmbH, Freising, Germany) equipped with a 100 mm² silicon drift detector for EDS (Oxford Instruments Ultim Max 100; Oxford Instruments GmbH NanoAnalysis, Wiesbaden, Germany). EDS is an analytical technique for elemental analysis of a specimen. To analyze the morphologies and chemical compositions, the Oxford Instruments Nanoanalysis AZtec 6.0 software was employed. The chemical composition was detected using an area scanning for 1 s at a beam energy of 15 keV.

2.4.2. Inductively coupled plasma mass spectroscopy (ICP-MS)

Approximately 50–200 mg of each carbon sample underwent microwave digestion in a reagent mixture of 6 ml of concentrated HNO₃ and 2 ml of H_2O_2 within an Anton Paar Multiwave PRO closed-vessel digestion system. This system was equipped with a 24HVT50 rotor (Anton Paar, Graz, Austria) and 30 ml PTFE vessels. The microwave

program was configured to attain a maximum temperature of 200 °C, which was reached within a ramp time of 10 min and then maintained for 15 min. The maximum microwave power utilized was 1500 W. Following digestion, the contents were filtered and appropriately diluted with 1% HNO₃. The concentrations of elements in the sample solutions were determined using an Agilent 7500ce ICP-QMS (Agilent Technologies, Tokyo, Japan). The analysis employed an external standard calibration with a multi-element standard solution mixture Merck VI (Merck Certipur, Darmstadt, Germany) in 1% HNO₃, utilizing internal standardization to ascertain the concentration of trace elements.

2.4.3. Raman spectroscopy

Raman spectroscopy is a spectroscopic method commonly employed for identifying the vibrational patterns of molecules and solid substances. Raman spectra were acquired using a WiTec alpha300R Raman spectrometer equipped with a diode-pumped solid-state laser emitting at a wavelength (λ) of 532 nm. A power of 1 mW was applied along with a 2 s iteration time and 100 accumulations. To facilitate laser focusing and sample observation before measurement, a confocal microscope was employed using a 50 \times long-working distance objective lens.

2.4.4. X-ray diffraction (XRD)

XRD is a scattering technique utilizing a single wavelength of X-rays as an incident beam. The intensity of the diffracted beam is recorded as a function of the scattering angle 2θ , or more generally, the scattering vector. XRD allows to investigate matter on the nanoscale to determine properties like the crystal structure of a given material as well as extract information for its purity.

XRD measurements were performed on a Bruker D8 Advance Eco equipped with Cu K\alpha radiation (~1.5418 Å wavelength) using a voltage of 40 kV and a current of 25 mA. Diffraction patterns were obtained using the Bragg-Brentano configuration with a continuous scan speed in a diffraction angle 2θ range of 10° – 90° with a step size of 0.02° and 1.2 s exposure time.

2.4.5. Gas sorption analysis: Brunauer-Emmett-Teller (BET) method

BET method is applied in gas sorption data (e.g., N₂ at 77 K) for determining the SSA of a given material. This method relies on the physical adsorption of gas molecules onto the surface of a solid material and takes into consideration the monolayer adsorbate capacity and the cross-sectional area of the adsorbate molecule. N₂ adsorption and desorption isotherms were collected at 77 K (-196 °C) using an Anton-Paar QuantaTec Autosorb-iQ3 manometric gas sorption analyzer and by employing ultra-pure (99.999%) N₂ as adsorbate, ultra-pure (99.999%) helium (He) gas for void volume calculations and liquid N₂ as cryogen. Prior to the tests, samples of ~150 mg were degassed under vacuum (10^{-6} mbar) at 250 °C for 24 h to remove physisorbed species and make the surface more accessible. The SSA was calculated by applying the multi-point BET method in the adsorption data for relative pressures (P/ P₀) between 0.05 and 0.3.

3. Results and discussion

The calculated data was utilized to analyze a model for the influencing factors, presented individually in the subsequent sections. In instances where two factors are examined in relation to the respective response, the third factor is held constant.

3.1. H_2 yield

An increase in the H_2 content within the product gas, and thus a higher H_2 yield, indicates enhanced process efficiency. Consequently, the dependence of this efficiency on various process parameters has been thoroughly investigated. The graphical representations in Fig. 5 reveal that an elevated CH₄ content in the plasma gas tends to reduce the H_2 yield, whereas higher current and arc lengths have a promoting



Fig. 5. The H₂ yield in relation to the interacting process parameters, shown as a contour map function of: a) Current vs. CH₄, b) Arc length vs. CH₄, and c) Arc length vs. Current.

effect, with higher current having a more significant influence. Specifically, at currents above 110 A, arc length becomes more relevant and plays a larger role. These trends are further demonstrated and confirmed in Fig. 6. CH₄ is identified as a gas component that influences the plasma arc, diminishing its stability and hindering it from reaching optimal conditions to provide the required energy for the reaction. In contrast, higher electric current levels contribute to increased power input, providing more energy for the process. Additionally, greater arc lengths create a more expansive environment for the reaction, resulting in a higher H₂ yield. Besides, higher arc lengths necessitate higher power input.

3.2. Power input

The power input is not a parameter that can be directly manipulated, but it can be controlled indirectly through the adjustment of the electric current and the arc length. Increasing the amperage leads to an increase in power, providing more energy for the pyrolysis reaction. As a result of electric current adjustments using the thyristor level, the amperage varies between 90 and 120 A, leading to a change in power within the range of 5–7 kW. Moreover, both a high CH₄ content and an extended arc length result in an increase in power input, as shown in Fig. 7. This is because CH₄ requires more energy for excitation and ionization, and a greater arc length also increases the voltage, necessitating higher power input. Fig. 8 shows the power input changes with the variables.

3.3. Stability time

The stability time is defined as the duration of the process before the first occurrence of arc disruption. This parameter serves as a crucial response for evaluating the stability of the process. During the tests, a maximum time of approximately 30 min was employed, which means that a test with a stability time of 30 min or slightly longer did not experience any arc disruptions.



Fig. 6. H₂ yield dependence on the process parameters: a) CH₄, b) Arc length, and c) Current.



Fig. 7. Power input in relation to the process parameter, shown as a contour map function of: a) Current vs. CH4, b) Arc length vs. CH4, and c) Arc length vs. Current.



Fig. 8. Power input dependence on the process parameters: a) CH₄, b) Arc length, and c) Current.

It is important to note that the stability time is influenced by various parameters. As previously mentioned, the employed plasma furnace is not tailored for the purpose of methane pyrolysis process. Even under optimal conditions, arc disruptions can still occur due to constraints such as the electrical unit limits or the reactor's geometry. Fig. 9 clearly illustrates that higher CH₄ content and an extended arc length significantly impact arc stability, leading to arc disruptions and finally shortening the stability time. The amperage and, consequently, the power input are restricted due to limitations within the electric unit. Overloading the electrical unit by pushing the amperage to its maximum limit results in overheating due to core losses and inadequate cooling. This necessitates an immediate shutdown of the unit to prevent damage, inevitably reducing stability time. The relations between the stability time and the process parameters are summarized in Figs. 9 and 10.

Another phenomenon that significantly affects process stability is the formation of carbon in the reaction zone. This disrupts the plasma arc from functioning optimally and introduces disturbances, by providing new surfaces for the plasma arc discharge. Further details on this aspect have been elucidated in a previous work [39].

4. Characterization of the produced carbon

The detailed findings, elaborated in subsequent sections, provide significant insights into the properties of the generated carbon. However, it is important to acknowledge the limitations imposed by the current experimental setup, which may constrain the extent of control over the carbon product. Therefore, a systematic investigation into the interplay of various influencing parameters on the variation in solid carbon properties necessitates a more controllable plasma setup.

4.1. SEM and EDS

The SEM images of the produced carbon samples are presented in Fig. 11. F(1-3) depict the filter-collected samples, exhibiting a fine



Fig. 9. Interaction of stability time with the process parameters, shown as a contour map function of: a) Current vs. CH₄, b) Arc length vs. CH₄, and c) Arc length vs. Current.



Fig. 10. Stability time dependence on the process parameters: a) CH₄, b) Arc length, and c) Current.

texture carried away by the gas flow. On the other hand, the C(1–3) series illustrates the chamber-collected samples. These samples exhibit larger sizes compared to the filter-collected samples and are attached to the inner surface of the reaction chamber, forming substantial dendritic particles that remain within the chamber. The dendritic and coral-like shapes are distinctly observable in the C(1–2) images, where higher magnification reveals the presence of nanocrystals and primary particles, as evident in C(3). In contrast, the filter-collected samples, as depicted in the F(1–3) images, appear to possess a fluffier texture.

These findings align with similar publications. For instance, Boutot et al. [8] described the resulting carbon of their plasma pyrolysis process as a mixture of amorphous and nanostructured material. Furthermore, as reported in the introduction section, the literature suggests that the carbon microstructure can vary in respect of the spot on which it is formed and grown. This also corresponds to the temperature and shape of the reactor.

When considering the application of carbon, particularly in sectors

like agriculture, avoiding harmful impurities is of utmost importance. Moreover, eliminating impurities can be challenging or even impossible at times, potentially leading to the oxidation of carbon and subsequent CO_2 emissions.

The EDS analysis aids in providing a preliminary assessment of potential impurities in the carbon. The results reveal a high-purity carbon, with negligible metal elements below 1 wt% present in the gas filter. Additional methods with higher precision are deemed necessary for a more accurate assessment of purity and elemental identification. Fig. 12 shows an example of the chemical analysis of a pure carbon sample collected from the reaction chamber.

4.2. ICP-MS

The ICP-MS analysis showed a highly pure carbon product with slight impurities, confirming the results from the EDS analysis. The results showed a carbon purity of 99.7% for the chamber-collected carbon



Fig. 11. SEM images of the carbon samples, obtained from filter F (1–3), and reaction chamber C (1–3). The magnifications of the images were $70 \times$ for (1), 600x for (2), and 1600x for (3).



Fig. 12. An example of the EDS analysis of a carbon sample from the reaction chamber. The entire image's area (600x) was scanned.

and 99.4% for the filter-collected carbon. The primary impurities identified include metals, which stem from the initial contamination of the filter. These elements are caused by the steelmaking and alloying tests done using the same filter and can thus be neglected. This can be confirmed additionally by comparing the samples from the filter to the pure ones from the reaction chamber.

4.3. Raman spectroscopy

The Raman spectra were compared to those obtained from a natural graphite powder of high carbon purity employed as a reference material in the current study. All carbon samples exhibit three characteristic bands in their Raman spectra (Fig. 13). These are the defect-activated D-band at ~1338 cm⁻¹, the graphitic G-band at ~1570 cm⁻¹, and the second order of the D-band, G'(2D)-band, at the higher frequencies (i.e., ~2700 cm⁻¹). However, in comparison with the D-band that requires

defects for its activation, the 2D band can be observed even in defectfree graphitic materials. These comparisons confirm the presence of graphitic-like structures with a low concentration of defects, as indicated by similar D/G intensity ratios for the pyrolysis-derived carbons. However, it is important to note that these carbon samples exhibit certain structural distinctions from perfect crystal graphite, primarily due to the presence of defects and vacancies, which are evident through the higher intensity of the D band in comparison to the reference graphite. Conversely, the presence of a G'(2D) band generally indicates a degree of order within the carbon material. Specifically, a single, unsplit G'(2D) peak suggests the development of a graphite-like structure on a two-dimensional lattice with an imperfect transition toward threedimensional graphitization. This observation is supported by the current studies, where the G'(2D) band does not show any splitting or shoulder features, suggesting the absence of a fully developed threedimensional graphite lattice [43]. The position and the intensity



Fig. 13. Raman spectra for the carbon collected from the filter and the reaction chamber versus a reference graphite powder of high carbon purity.

values of the samples are listed in Table 2. Notably, the intensity ratio of the D and G bands (I_D/I_G) increases by progressing from the chamber-collected carbon to the filter-collected carbon, implying an increase in defects [44]. Meanwhile, the reference graphite sample has the lowest I_D/I_G . Based on the values given in Table 2, the reference graphite is characterized by the most ordered and defect-reduced structure. Comparing the carbon samples obtained by pyrolysis, the defect concentration is higher for the filter-collected carbon in contrast to chamber-collected carbon. This phenomenon can be elucidated by the elevated temperature inside the reactor, which promotes better crystallization compared to that occurring in the filter.

4.4. XRD

X-ray diffractograms for all the studied samples are presented in Fig. 14. They revealed crystalline structures comparable to that of graphitic carbon (JCPDS card no. 75-1621), while no crystalline impurities were detected for the pyrolysis-derived carbons. All XRD patterns showed a dominant peak at $2\theta \sim 26^{\circ}$ related to the (002) graphitic reflection, followed by much less intense peaks at $\sim 43^{\circ}$, $\sim 54^{\circ}$, 77° , and 83°, representing the (100)/(101),(004), (110), and (112) crystal planes, respectively. Generally, the narrower and higher the (002) peak, the better the orientation of the aromatic layer. The narrower and higher the peak (100)/(101), the larger the size of the aromatic layer. Both carbon materials are characterized by rather narrow peaks (002), while only the carbon from the chamber is characterized by a larger size of aromatic layers compared to carbon from the filter. Diffraction peaks corresponding to the (100)/(101), (004), and (110) planes of graphitic carbon begin to appear at very high temperatures, expected in the reactor. These peaks are more pronounced for chamber-collected carbon, indicating a more ordered structure, and practically disappear for filter-collected carbon, indicating that the carbon from the filter was less subjected to the very high temperatures. The (112) peak indicates a complex crystalline structure or the presence of multiple phases within the carbon, which is slightly visible in the reference graphite sample.

Table 2

Results of Raman spectroscopy.



Fig. 14. X-ray diffractograms for the carbon collected from the filter and the reaction chamber versus a reference graphite powder of high carbon purity.

However, this peak is absent in both carbon samples collected from the filter and the chamber.

4.5. BET SSA

Selective carbon samples were chosen for assessing their BET SSA. It can be observed that the fine carbon from the filter with a smaller particle size has a higher BET SSA compared to the chamber-collected samples.

To evaluate the obtained results, it is essential to commence by reviewing the findings presented in the literature [32–34,45]. Kim et al. [32] reported a BET SSA of 60 m^2/g for the carbon from the cyclone and $385 \text{ m}^2/\text{g}$ for the samples in the filter. Another study [33] reported 42–49 m²/g SSA for nanostructured sheet-like carbon material. Fulcheri et al. [34] reported a BET SSA of 90–110 m^2/g . In this study, the filter-collected carbon samples showed a wide range of BET SSA values between 40 and 170 m²/g. This is a considerably high BET SSA compared to the measured BET SSA of the reference graphite powder sample, which was 27 m^2/g . However, it is essential to highlight that the chamber-collected carbon samples exhibited a lower BET SSA, ranging from approximately 7 to 30 m^2/g . As discussed in the introduction section, these differences in SSA can be attributed to the finer and smaller particle sizes observed in the filter-collected samples compared to those of the reactor. Furthermore, the increased defect concentration identified through Raman analysis may contribute to the higher SSA

Samples	D band		G band		G'(2D) band		I_D/I_G					
	Position (cm ⁻¹)	Intensity (a.u.)	Position (cm ⁻¹)	Intensity (a.u.)	Position (cm ⁻¹)	Intensity (a.u.)						
Filter carbon	1344.96	0.74	1574.16	1	2679.65	0.41	0.74					
Chamber carbon	1344.97	0.51	1574.16	1	2683.61	0.38	0.51					
Graphite reference	1340.26	0.27	1565.03	1	2697.69	0.42	0.27					

observed. Fig. 15 shows the N_2 adsorption and desorption isotherms at 77 K for the selected samples. Additionally, the corresponding BET SSA values are mentioned in the figure. No significant correlation between the process parameters and the BET SSA values could be found.

5. Summary and conclusions

This study explores the use of thermal plasma technology for hydrogen and carbon production through methane pyrolysis. Utilizing a DC-transferred plasma arc furnace, thirteen pyrolysis experiments were conducted, guided by a design of experiment tool. The research focused on three primary variables: the CH₄ content in the plasma gas, the electric current and the arc length, all of which varied within a specific range. The results showed a high H₂ yield, ranging from 67% to 100%. However, the process demonstrated instability, which was attributed to the reactor's design and constraints previously discussed in another study [39]. A comprehensive analysis of the H₂ yield, power input, and stability time provided valuable insights into the interaction of these parameters.

An increase in the CH_4 content in the plasma gas was found to decrease plasma arc stability, interrupting the process. This issue could be mitigated by increasing the power input, but at the cost of higher operational expenses. Longer arc lengths were associated with a greater risk of arc disruption, which could be offset by increasing the power input. While longer arcs created a larger hot reaction zone, they also necessitated higher power input to enhance H_2 yield and prolong stable processing time. However, this approach may lead to increased thermal stress and accelerated erosion of the graphite electrodes.

The characterization of the produced carbon involved various analytical techniques aimed at identifying and quantifying morphological, microstructural, chemical, and surface area features. SEM analyses revealed distinct microstructural differences between samples collected from the gas filter and those from the reaction chamber, with the former displaying finer textures and the latter exhibiting larger sizes and dendritic particles. Raman spectroscopy confirmed the presence of crystalline graphite-like structures with low defect concentrations in all examined carbon samples. XRD further supported these findings, indicating crystalline structures comparable to graphitic carbon. EDS and ICP-MS analyses confirmed high-purity carbon with slight impurities, primarily from initial filter contaminations, which can be neglected when comparing samples from the filter to pure ones from the chamber. Gas sorption measurements highlighted significant variations, with filter-collected samples showing higher BET SSA values between 40 and $170 \text{ m}^2/\text{g}$ compared to chamber-collected samples of 7–30 m²/g, which correlate to their smaller particle size and higher number of defects. These differences underscore the importance of considering the source and collection method when characterizing carbon samples. The comprehensive characterization provides valuable insights into the properties of the produced carbon, laying a foundation for further research and development in this field, employing advanced experimental setups to unravel the intricate relationships between process parameters and carbon properties. Such endeavors will not only enhance our fundamental understanding but also contribute to optimizing the plasma pyrolysis process for producing carbon materials with desired properties.

CRediT authorship contribution statement

Oday Daghagheleh: Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. Johannes Schenk: Writing – review & editing, Writing – original draft, Supervision, Investigation, Conceptualization. Heng Zheng: Writing – review & editing. Michael Andreas Zarl: Writing – review & editing, Methodology, Investigation. Manuel Farkas: Writing – review & editing, Methodology, Investigation. Daniel Ernst: Writing – review & editing. Lina Kieush: Writing – review & editing, Investigation. Markus Lehner:



Fig. 15. Results of adsorption and desorption experiments using N_2 at 77 K. Solid symbols denote the adsorption branch; empty symbols denote the desorption branch of the isotherm.

Writing – review & editing, Supervision. **Nikolaos Kostoglou:** Writing – review & editing, Investigation. **Robert Obenaus-emler:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research received no external funding and is directly funded by Montanuniversität Leoben. We extend our sincere gratitude to our esteemed colleagues for their invaluable assistance and unwavering support in refining carbon characterization methodologies and elucidating their interpretations. Special thanks are due to Bernd Lederhaas of the Chair of Ferrous Metallurgy, Donata Bandoniene and Thomas C. Meisel of the Chair of General and Analytical Chemistry, as well as Florian Knabl, Velislava Terziyska, and Anna Hofer Roblyek from the Chair of Functional Materials and Materials Systems, at Montanuniversität Leoben. We are grateful to Christian Mitterer and Oskar Paris from Montanuniversität Leoben for providing access to the gas sorption analyzer.

References

- European Commission. The European Green 2050: boosting the economy, improving people's health and quality of life, caring for nature, and leaving no one behind. 2019.
- [2] Islam A, Islam T, Mahmud H, Raihan O, Islam MS, Marwani HM, et al. Accelerating the green hydrogen revolution: a comprehensive analysis of technological advancements and policy interventions. Int J Hydrogen Energy 2024;67:458–86. https://doi.org/10.1016/j.ijhydene.2024.04.142.
- [3] Arsad SR, Ker PJ, Hannan MA, Tang SG, R SN, Chau CF, et al. Patent landscape review of hydrogen production methods: assessing technological updates and innovations. Int J Hydrogen Energy 2024;50:447–72. https://doi.org/10.1016/j. ijhydene.2023.09.085.
- [4] Dermühl S, Riedel U. A comparison of the most promising low-carbon hydrogen production technologies. Fuel 2023;340:127478. https://doi.org/10.1016/j. fuel.2023.127478.
- [5] Da Silva Veras T, Mozer TS, Da Costa Rubim Messeder dos Santos D, Da Silva César A. Hydrogen: trends, production and characterization of the main process worldwide. Int J Hydrogen Energy 2017;42(4):2018–33. https://doi.org/10.1016/ j.ijhydene.2016.08.219.

O. Daghagheleh et al.

- [6] Hermesmann M, Müller TE. Green, turquoise, blue, or grey? Environmentally friendly hydrogen production in transforming energy systems. Prog Energy Combust Sci 2022;90:100996. https://doi.org/10.1016/j.pecs.2022.100996.
- [7] Hefner R. Toward sustainable economic growth: the age of energy gases. Int J Hydrogen Energy 1995;20(12):945–8. https://doi.org/10.1016/0360-3199(95) 00043-D.
- [8] Boutot T, Bullerwell J, Liu Z, Niu W, Whidden TK, Yang Y. Hydrogen and nanostructured carbon by plasma decomposition of natural gas. ECS Trans 2009;16 (50):155–66. https://doi.org/10.1149/1.3157945.
- [9] Cheon S, Byun M, Lim D, Lee H, Lim H. Parametric study for thermal and catalytic methane pyrolysis for hydrogen production: techno-economic and scenario analysis. Energies 2021;14(19):6102. https://doi.org/10.3390/en14196102.
- [10] Alhamed H, Behar O, Saxena S, Angikath F, Nagaraja S, Yousry A, et al. From methane to hydrogen: a comprehensive review to assess the efficiency and potential of turquoise hydrogen technologies. Int J Hydrogen Energy 2024;68: 635–62. https://doi.org/10.1016/j.ijhydene.2024.04.231.
- [11] Sanyal A, Malalasekera W, Bandulasena H, Wijayantha K. Review of the production of turquoise hydrogen from methane catalytic decomposition: optimising reactors for Sustainable Hydrogen production. Int J Hydrogen Energy 2024;72:694–715. https://doi.org/10.1016/j.ijhydene.2024.05.397.
- [12] International Energy Agency. Net Zero Roadmap: a global pathway to keep the 1.5 °C goal in reach. 2023.
- [13] IEA International Energy Agency. Global hydrogen review. 2022.
- [14] Chan YH, Chan ZP, Lock SSM, Yiin CL, Foong SY, Wong MK, et al. Thermal pyrolysis conversion of methane to hydrogen (H2): a review on process parameters, reaction kinetics and techno-economic analysis. Chin Chem Lett 2024; 35(8):109329. https://doi.org/10.1016/j.cclet.2023.109329.
- [15] Fulcheri L, Fabry F, Takali S, Rohani V. Three-phase AC arc plasma systems: a review. Plasma Chem Plasma Process 2015;35(4):565–85. https://doi.org/ 10.1007/s11090-015-9619-8.
- [16] Scheiblehner D, Antrekowitsch H, Neuschitzer D, Wibner S, Sprung A. Hydrogen production by methane pyrolysis in molten Cu-Ni-Sn alloys. Metals 2023;13(7): 1310. https://doi.org/10.3390/met13071310.
- [17] Neuschitzer D, Scheiblehner D, Antrekowitsch H, Wibner S, Sprung A. Methane pyrolysis in a liquid metal bubble column reactor for CO₂-free production of hydrogen. Energies 2023;16(20):7058. https://doi.org/10.3390/en16207058.
- [18] Schneider S, Bajohr S, Graf F, Kolb T. Verfahrensübersicht zur Erzeugung von Wasserstoff durch Erdgas-Pyrolyse. Chem Ing Tech 2020;92(8):1023–32. https:// doi.org/10.1002/cite.202000021.
- [19] Dagle R, Dagle V, Bearden M, Holladay J, Krause T, Ahmed S. An overview of natural gas conversion technologies for co-production of hydrogen and valueadded solid carbon products. U.S. Department of Energy Fuel Cell Technologies Office; 2017.
- [20] Keipi T, Hankalin V, Nummelin J, Raiko R. Techno-economic analysis of four concepts for thermal decomposition of methane: reduction of CO 2 emissions in natural gas combustion. Energy Convers Manag 2016;110:1–12. https://doi.org/ 10.1016/j.enconman.2015.11.057.
- [21] Gautier M, Rohani V, Fulcheri L. Direct decarbonization of methane by thermal plasma for the production of hydrogen and high value-added carbon black. Int J Hydrogen Energy 2017;42(47):28140–56. https://doi.org/10.1016/j. ijhydene.2017.09.021.
- [22] Kalamaras CM, Efstathiou AM. Hydrogen production technologies: current state and future developments. Conference Papers in Energy 2013;2013(3):1–9. https:// doi.org/10.1155/2013/690627.
- [23] Abbas HF, Wan Daud W. Hydrogen production by methane decomposition: a review. Int J Hydrogen Energy 2010;35(3):1160–90. https://doi.org/10.1016/j. ijhydene.2009.11.036.
- [24] Raza J, Khoja AH, Anwar M, Saleem F, Naqvi SR, Liaquat R, et al. Methane decomposition for hydrogen production: a comprehensive review on catalyst selection and reactor systems. Renew Sustain Energy Rev 2022;168:112774. https://doi.org/10.1016/j.rser.2022.112774.
- [25] Patlolla SR, Katsu K, Sharafian A, Wei K, Herrera OE, Mérida W. A review of methane pyrolysis technologies for hydrogen production. Renew Sustain Energy Rev 2023;181:113323. https://doi.org/10.1016/j.rser.2023.113323.

- [26] Wnukowski M. Methane pyrolysis with the use of plasma: review of plasma reactors and process products. Energies 2023;16(18):6441. https://doi.org/ 10.3390/en16186441.
- [27] Solonenko OP. Thermal plasma torches and technologies. Plasma torches: basic studies and design. Institute of theoretical and applied mechanics. Novosibirsk: Siberian Branch of the Russian Academy of Sciences; 2000.
- [28] Fincke JR, Anderson RP, Hyde TA, Detering BA. Plasma pyrolysis of methane to hydrogen and carbon black. Ind Eng Chem Res 2002;41(6):1425–35. https://doi. org/10.1021/ie010722e.
- [29] Lee YH, Oh J-H, Choi S. Evaluation of process conditions for methane pyrolysis applying the triple thermal plasma system. Int J Hydrogen Energy 2023;48(70): 27127–36. https://doi.org/10.1016/j.ijhydene.2023.03.427.
- [30] Li T, Rehmet C, Cheng Y, Jin Y, Cheng Y. Experimental comparison of methane pyrolysis in thermal plasma. Plasma Chem Plasma Process 2017;37(4):1033–49. https://doi.org/10.1007/s11090-017-9806-x.
- [31] Mašláni A, Hrabovský M, Křenek P, Hlína M, Raman S, Sikarwar VS, et al. Pyrolysis of methane via thermal steam plasma for the production of hydrogen and carbon black. Int J Hydrogen Energy 2021;46(2):1605–14. https://doi.org/10.1016/j. ijhydene.2020.10.105.
- [32] Kim H, Kim H, Kim S, Lee S, Kim J. Hydrogen production in methane decomposition reactor using solar thermal energy. Appl Sci 2021;11(21):10333. https://doi.org/10.3390/app112110333.
- [33] Kim KS, Hong SH, Lee K-S, Ju WT. Continuous synthesis of nanostructured sheetlike carbons by thermal plasma decomposition of methane. IEEE Trans Plasma Sci 2007;35(2):434–43. https://doi.org/10.1109/TPS.2007.892556.
- [34] Fulcheri L, Rohani V-J, Wyse E, Hardman N, Dames E. An energy-efficient plasma methane pyrolysis process for high yields of carbon black and hydrogen. Int J Hydrogen Energy 2022. https://doi.org/10.1016/j.ijhydene.2022.10.144.
- [35] Naseri Seftejani M, Schenk J, Zarl MA. Reduction of haematite using hydrogen thermal plasma. Materials 2019;12(10). https://doi.org/10.3390/ma12101608.
- [36] Zarl MA, Farkas MA, Schenk J. A study on the stability fields of arc plasma in the HPSR process. Metals 2020;10(10):1394. https://doi.org/10.3390/met10101394.
- [37] Zarl MA, Ernst D, Cejka J, Schenk J. A new methodological approach to the characterization of optimal charging rates at the hydrogen plasma smelting reduction process Part 1: method. Materials 2022;15(14). https://doi.org/ 10.3390/ma15144767.
- [38] Ernst D, Zarl MA, Cejka J, Schenk J. A new methodological approach on the characterization of optimal charging rates at the hydrogen plasma smelting reduction process Part 2: results. Materials 2022;15(12). https://doi.org/10.3390/ ma15124065.
- [39] Daghagheleh O, Schenk J, Zarl MA, Lehner M, Farkas M, Zheng H. Feasibility of a plasma furnace for methane pyrolysis: hydrogen and carbon production. Energies 2024;17:167. https://doi.org/10.3390/en17010167.
- [40] Keipi T, Tolvanen KE, Tolvanen H, Konttinen J. Thermo-catalytic decomposition of methane: the effect of reaction parameters on process design and the utilization possibilities of the produced carbon. Energy Convers Manag 2016;126:923–34. https://doi.org/10.1016/j.enconman.2016.08.060.
- [41] Patlolla SR, Katsu K, Sharafian A, Wei K, Herrera OE, Mérida W. A review of methane pyrolysis technologies for hydrogen production. Renew Sustain Energy Rev 2023;181:113323. https://doi.org/10.1016/j.rser.2023.113323.
- [42] Pristavita R, Mendoza-Gonzalez N-Y, Meunier J-L, Berk D. Carbon blacks produced by thermal plasma: the influence of the reactor geometry on the product morphology. Plasma Chem Plasma Process 2010;30(2):267–79. https://doi.org/ 10.1007/s11090-010-9218-7.
- [43] Cuesta A, Dhamelincourt P, Laureyns J, Martínez-Alonso A, Tascón JMD. Raman microprobe studies on carbon materials. Carbon 1994;32(8):1523–32. https://doi. org/10.1016/0008-6223(94)90148-1.
- [44] Rosenburg F, Ionescu E, Nicoloso N, Riedel R. High-temperature Raman spectroscopy of nano-crystalline carbon in silicon oxycarbide. Materials 2018;11 (93). https://doi.org/10.3390/ma11010093.
- [45] Lina Kieush, Johannes Schenk, Andrii Koveria, Gerd Rantitsch, Andrii Hrubiak and Horst Hopfinger. Utilization of renewable carbon in electric arc furnace-based steel production: comparative evaluation of properties of conventional and nonconventional carbon-bearing sources.