

Mathematical modelling of sequential DRM and catalyst regeneration in a fixed-bed reactor

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Abstract

Dry reforming of methane is an attractive route for syngas production because it enables the simultaneous utilisation of methane and carbon dioxide. However, its practical application is limited by high energy demand, catalyst deactivation and, in particular, carbon deposition on the catalyst surface. In this work, a mathematical model of sequential dry reforming of methane and CO₂-assisted catalyst regeneration in a fixed-bed reactor is proposed. The carbon formed during the reforming stage is treated not only as a deactivating deposit, but also as a reactive intermediate that can be converted into carbon monoxide during the subsequent regeneration step. The axial distribution of carbon obtained from the DRM model is used as the initial condition for the transient regeneration model. To avoid dependence of the total carbon mass on the spatial discretisation adopted for regeneration, the carbon distribution from the DRM stage is recalculated into the mass of carbon assigned to reactor intervals Δm_C , and then transferred to the regeneration grid using a local linear carbon-mass density reconstructed by cubic spline interpolation and integrated numerically over the new grid intervals. The regeneration model describes transient changes in CO₂ and CO concentrations and in the local mass of deposited carbon along the reactor. A thermodynamic constraint based on the reaction quotient and the equilibrium constant of the reverse Boudouard reaction is introduced to limit carbon gasification to conditions favourable for CO formation. The resulting system of equations is solved numerically using the method of lines and a stiff ODE solver. The influence of spatial grid discretisation is analysed, and a discretisation level is selected to strike a balance between numerical accuracy and computational cost. Regeneration simulations are performed over a temperature range of 973 to 1270 K. The results show that the proposed model enables the local course of catalyst regeneration to be followed, preserves the carbon mass balance when the regeneration grid is changed, and provides a basis for assessing CO₂-assisted regeneration as part of cyclic DRM-regeneration operation.

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1. INTRODUCTION

Dry reforming of methane (DRM) is one of the more attractive methods of syngas production, as it enables the simultaneous utilisation of two greenhouse gases: methane and carbon dioxide. Unlike conventional steam reforming, this process does not require steam as an oxidising agent for the carbon in methane; instead, it uses CO₂. This makes it particularly attractive in the context of emission reduction, biogas utilisation and the production of an H₂/CO mixture with a molar ratio close to unity. At the same time, DRM remains a technologically challenging process because it requires high temperatures, is strongly endothermic, and is limited in practical application mainly by catalyst deactivation due to carbon deposition and by its high energy demand.

Agún and Abanades (2025) indicate that DRM has considerable potential for reducing greenhouse gas emissions, but has not yet been implemented industrially, mainly because of coke formation, high energy demand, and problems related to catalyst durability and cost. The authors emphasise that the attractiveness of the process increases when the heat required for the reaction is supplied from low-emission sources and

when biogas or biomethane is used as the feedstock. This is an important argument for the present work, as it shows that the analysis of catalyst regeneration and the carbon balance is not a secondary issue, but one of the conditions for the practical use of DRM as a more environmentally favourable technology for syngas production. In their review, Aramouni and co-workers (Aramouni et al., 2018) analyse the design of DRM catalysts, showing that the activity and stability of the system depend simultaneously on the active metal, support and promoters. The authors point out that DRM converts CH₄ and CO₂ into syngas with an H₂/CO ratio close to 1, but that the process requires high temperature and rapid carbon formation leads to catalyst deactivation. From the perspective of the present work, catalyst design must consider not only initial activity but also resistance to coking and the ability to maintain long-term stability. In their review, Wang et al. (2024) present a current overview of nickel-based catalysts used in DRM and indicate that Ni is attractive because of its high activity and low cost, but that its long-term stability is limited by sintering and carbon deposition. The authors also emphasise that current industrial steam reforming remains the dominant method of syngas production, but its wider use is associated with high costs and a high H₂O/CH₄ ratio. In this



context, DRM may be particularly beneficial in regions rich in natural gas but limited in water availability. This supports the view that DRM may represent a more environmentally favourable alternative to conventional steam-based processes, provided that the problems of coking and catalyst regeneration are solved. Wang and co-workers (Wang et al., 2024) also discuss the mechanisms of carbon deposit formation and removal on nickel catalysts. They indicate that catalyst durability depends on the balance between carbon generation and removal, and that CO₂ activation can provide oxygen species capable of gasifying surface carbon deposits. This directly justifies modelling the catalyst regeneration step using CO₂ as a process that competes with coke accumulation. Zhao and co-workers (Zhao et al., 2025) present a modern approach to electrified DRM, in which an electric current passed through a conductive Ni-La₂O₃/AC catalyst enabled conversions close to equilibrium and stable operation for at least 120 h. The authors emphasise that conventional DRM may paradoxically have a positive emission balance if the thermal energy is supplied by fossil fuel combustion. In contrast, electrification powered by low-emission electricity may lead to a net CO₂-negative process. This article strengthens the environmental justification for the present work, as it shows that the future of DRM may depend not only on catalyst design, but also on the method of energy supply and on controlling carbon-related reactions on the catalyst surface.

The work of Snoeck, Froment and Fowles (Snoeck et al., 2002) provides an important kinetic basis for the problem of catalyst regeneration, as it analyses filamentous carbon formation on a nickel catalyst through the Boudouard reaction and its gasification by CO₂, H₂ and steam. The authors indicate that carbon on Ni catalysts may occur as filaments or whiskers, and that its formation and gasification are complex phenomena involving carbon formation on the Ni surface, diffusion through the metal particle, and the growth or shrinkage of the carbon filament. This article is particularly valuable because it shows that the description of catalyst regeneration should not be based solely on thermodynamics, but also requires a kinetic treatment. Osazuwa and Ng (2025) focus directly on carbon formed during DRM, including its forms, identification, and quantification. The authors indicate that carbon deposition is primarily driven by methane decomposition and the Boudouard reaction, and that the resulting carbon may be graphitic, amorphous, or filamentous, with each form exhibiting a different susceptibility to regeneration. This review strongly justifies the need for the present work, as it shows that without knowledge of the amount and nature of carbon deposited on the catalyst, it is not possible to design strategies for its removal rationally. It was also noted (see Osazuwa and Ng, 2025) that the performance of DRM is limited more by persistent carbon deposition than by the transient formation of reactive carbon species. In their view, properly identifying the type of deposit is the first step towards effective design of carbon gasification and catalyst regeneration. This is consistent with the concept that the axial distribution

of carbon in the reactor is not treated solely as a by-product of the simulation, but as the initial variable for the subsequent step, i.e., regeneration in a CO₂ atmosphere. Hosseinpour and co-workers (Hosseinpour et al., 2025) directly demonstrate a strategy for regenerating DRM catalysts using pure CO₂. In their work, regeneration of a Ni-Zr catalyst through the reverse Boudouard reaction removed a substantial fraction of deposited coke. It simultaneously led to Ni redispersion and the formation of a more active catalyst state with more favourable Ni/ZrO₂ phase boundaries. This article is one of the strongest arguments for the concept of cyclic operation, because it experimentally confirms that CO₂ can act not only as a DRM reactant, but also as a catalyst-regenerating agent. Hosseinpour and co-workers (Hosseinpour et al., 2025) also show that CO₂ regeneration may be more beneficial than conventional oxidative regeneration because it selectively removes carbon deposits without deep oxidation or degradation of the catalyst's metallic state. The authors indicate that CO₂ regeneration improves the Ni particle-size distribution, increases the number of coke-resistant active sites and enables higher activity to be maintained in subsequent DRM cycles. This provides a strong justification for simulating cyclic reforming-regeneration operation, in which the carbon removal step is treated as an integral part of the process rather than only as an emergency procedure. Lewak (2025) showed that mathematical modelling of a fixed-bed reactor can be used to determine the influence of wall temperature and total pressure not only on CH₄ and CO₂ conversion, but also on the total mass of carbon deposited on the catalyst. That study indicated that carbon deposition is one of the main limitations of the DRM process and that simulation results should be analysed carefully, as many kinetic models do not explicitly account for catalyst deactivation. This provides a direct basis for developing a new model in which the calculated axial carbon distribution serves as the initial condition for the regeneration step.

Based on the cited studies, it can be argued that further development of DRM requires a departure from the sole treatment of carbon deposition as an undesirable deactivation phenomenon. A more useful approach is to analyse the balance between carbon formation during the reforming step and carbon removal during the regeneration step, particularly when CO₂ is used as the regenerating agent. In this approach, the deposited carbon can be treated as a transient component of the system, which in the reverse Boudouard reaction:



can be converted into carbon monoxide, thereby increasing the amount of gaseous product and partially restoring the catalyst surface. Therefore, the present work aims to numerically analyse the feasibility of carrying out DRM in a sequential mode, comprising a methane reforming step with CO₂ and a catalyst regeneration step using CO₂. Particular attention is paid to the spatial distribution of carbon deposited along the reactor and to its subsequent removal via the reverse

Boudouard reaction. This approach may represent a step towards more sustainable syngas production and, in the longer term, towards hydrogen or hydrogen-rich mixtures, with reduced dependence on conventional steam reforming.

2. Review of kinetic models for carbon gasification with carbon dioxide

Ergun's work (Ergun, 1956) was among the first to show that the reaction of carbon dioxide with carbon is a complex, heterogeneous process in which active sites on the carbon surface and oxygen exchange between the gas and solid phases play key roles. His work shows that the gasification rate depends not only on temperature but also on the number of available reaction sites and the composition of the gas phase, especially the presence of CO, which may inhibit the reaction. This is of key importance in the mathematical description of the process because the structure of the carbon deposited on the catalyst will affect the reaction's kinetic model. This is an important conclusion in the context of catalyst regeneration after DRM, as it shows that deposited carbon should not be treated as a homogeneous mass, but as a material with a specific surface reactivity. Dai and co-workers (Dai et al., 2021) presented the Boudouard reaction as a route for converting CO₂ into CO using semi-coke in a fixed-bed reactor, comparing conventional and microwave heating. They showed that the course of gasification strongly depends on temperature, the method of energy supply, particle size, CO₂ flow rate and the presence of catalytic additives, i.e. parameters that may also be analysed in simulations of catalyst regeneration. For the present work, it is particularly important that carbon gasification can be described in a simplified way by relating the reaction rate to carbon conversion, thereby allowing the deposit loss to be related to the duration of the regeneration step. Mo and co-workers (Mo et al., 2023) transferred the problem to an area directly related to DRM, as they analysed the structure and removal of carbon deposited on Ni–Al₂O₃ catalysts after methane reforming with carbon dioxide. This is therefore the type of catalyst that formed the basis for determining the kinetic model of the DRM reaction (see Cherbański et al., 2021). The kinetic model enabled the determination of the amount of carbon deposited on the catalyst during the process (see Lewak, 2025).

In the work of Mo et al. (2023), the main form of the deposit was filamentous carbon, although amorphous and more ordered/graphitised forms were also present. Their contribution depended on the catalyst preparation method and affected catalyst stability. This article justifies the use of kinetic modelling in catalyst regeneration by showing that the removal of carbon deposits is a temperature-dependent process that depends on carbon structure and the catalyst's properties. Alsawadi and co-workers (Alsawadi et al., 2025) showed that the reactivity of carbon gasification by CO₂ depends on many features of the carbon material, including porosity, mineral composition, CO₂ chemisorption, morphology and surface structure. Their

work is particularly useful for the present simulation, as it allows gasification to be treated as a process governed by relationships among carbon conversion, temperature, and material properties, without the need to reproduce the deposit's microscopic structure fully. The results of Mo et al. (2023), therefore, justify the choice of the model from Alsawadi et al. (2025), because the morphology of the carbon formed during DRM indicates that an approximate model is required, but one linked to the actual amount of carbon remaining on the catalyst. It should be emphasised, however, that the parameters of this model should in reality depend on the nature of the carbon deposited on the catalyst, its degree of ordering, the contribution of amorphous and graphitised forms, and the composition and structure of the catalyst itself. The kinetic model used in this work is a tool for assessing the feasibility of the reforming-regeneration process, and not a universal kinetic description of the gasification of every carbon deposit.

3. Kinetic model of the carbon gasification reaction

In this work, the kinetics of carbonaceous deposit removal by carbon dioxide were described using literature data on the gasification of coal char (CC) reported by Alsawadi et al. (2025). The choice of this sample results from the nature of the carbonaceous deposit formed during dry reforming of methane on nickel catalysts. The carbon deposited in the DRM process is not a biomass-derived material, but a product of surface reactions occurring on the active Ni/NiO–Al₂O₃ phase. Therefore, its structure may be closer to that of more ordered, less reactive forms of carbon than to biochar or hydrochar. Experimental data on carbonaceous deposits formed during CO₂ reforming of CH₄ on Ni–Al₂O₃ catalysts indicate that the dominant form of the deposit is filamentous carbon. Mo et al. (2023) showed that the carbon deposit on Ni–Al₂O₃ catalysts after stability tests consisted mainly of filamentous carbon, and that its accumulation could lead to pore blockage and deterioration of catalytic properties. These authors also indicated that graphitic carbon is among the more inert deposit forms and requires higher temperatures for removal. In contrast, carbon nanotubes and filamentous carbon may block catalyst pores (Mo et al., 2023). For this reason, the direct use of kinetic parameters determined for biochars or hydrochars could lead to an overestimation of the catalyst regeneration rate. In the work of Alsawadi (Alsawadi et al., 2025), hydrochar exhibited particularly high reactivity, which was strongly associated with the presence of mineral components and its ability to chemisorb CO₂. The authors showed that after demineralisation, hydrochar reactivity decreased significantly, indicating the dominant role of ash components in its gasification (Alsawadi et al., 2025). Such properties do not necessarily correspond to the carbonaceous deposit formed on a Ni–Al₂O₃ catalyst during DRM. The selection of data for the CC sample is further justified by the model-fitting results reported by Alsawadi et al. (2025). The authors compared

three CO₂ gasification models: the volumetric model (VM), the grain model (GM) and the random pore model (RPM). For biochars and hydrochar, the best fit was usually obtained with the RPM model, whereas for the CC sample, it was obtained with the VM model. The authors emphasised that this indicates a different gasification mechanism for coal char compared with biomass-derived materials (Alsawadi et al., 2025).

The kinetic model of the carbon gasification reaction has one important advantage: it is indirectly based on the mass of carbon deposited on the catalyst. The kinetic model also includes the mass of carbon remaining after the reaction, reflecting that the reverse Boudouard reaction is reversible and cannot lead to complete gasification of the carbon present on the catalyst under all conditions. The kinetic model proposed by Alsawadi (Alsawadi et al., 2025) has the following form:

$$\frac{dX_m}{dt} = A_0 e^{-\frac{E_a}{RT}} (1 - X_m) \quad (2)$$

$$\text{where: } X_m = \frac{m_{C0} - m_C(t)}{m_{C0} - m_C^*}$$

The kinetic equation given in Eq. (2) assumes that the interaction of the reacting gas with the solid material occurs relatively uniformly within the accessible volume of the particle or deposit, and that the reaction rate decreases proportionally to the amount of carbon remaining. This description is simpler than the RPM model and may be a more appropriate first approximation for a carbonaceous deposit with an ambiguously defined pore structure. In the article by Alsawadi et al. (2025), the following VM model parameters were reported for the CC sample: $E_a = 193.6$ kJ/mol, $A_0 = 26903.2$ s⁻¹.

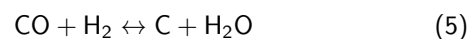
The choice of the CC data should therefore be treated as a conservative approach. Compared with hydrochar or reactive biochars, coal char is characterised by lower reactivity and a different gasification mechanism. This is important in modelling catalyst regeneration, because adopting a material that is too reactive could artificially shorten the predicted time required to remove coke from the catalyst surface. At the same time, it should be emphasised that CC is not an ideal equivalent of coke formed on a nickel catalyst, but rather the best approximation among the materials analysed in the study from which the kinetic model was taken. The real deposit may contain amorphous, filamentous and graphitic fractions, the proportions of which depend on temperature, reactor operating time, gas composition and catalyst properties, as confirmed by the results of Mo et al. (2023) for Ni–Al₂O₃ catalysts after CO₂ reforming of CH₄. The use of parameters for CC should therefore be treated as an initial modelling step. Ultimately, the kinetic parameters should be experimentally verified for the actual carbonaceous deposit formed during dry reforming of methane on a NiO/Al₂O₃ catalyst. However, during the conceptual model development stage, the choice of the CC sample avoids an overly optimistic description of the regeneration rate. It better reflects the lower reactivity

of carbonaceous deposits that may form during long-term operation of a nickel catalyst.

For numerical simulations describing carbon gasification, the kinetic model (see Eq. (2)) was adopted as the rate of carbon mass gasification per unit time:

$$\frac{dm_C}{dt} = -A_0 e^{-\frac{E_a}{RT}} (m_C - m_C^*) \quad (3)$$

In the kinetic model proposed by Alsawadi et al. (2025), the term $(m_C(t) - m_C^*)$ limits the carbon gasification rate because it accounts for the amount of solid material that can still react with CO₂. In the case of samples analysed by thermogravimetry, the quantity m_C^* may be associated with the presence of a non-gasifiable residue resulting from the varied origin of the carbonaceous material, its mineral composition and the contribution of less reactive fractions. In the present work, the physical situation is different. The carbon present on the catalyst is not a primary material of heterogeneous origin but a product of chemical reactions during the dry reforming of methane. The carbonaceous deposit forms via surface reactions that produce a carbon phase on the nickel catalyst. Therefore, in the conceptual model, the entire carbon mass determined in the DRM step was assumed to constitute a potentially reactive deposit capable of undergoing gasification in the presence of CO₂. Consequently, $m_C^* = 0$ was adopted. This assumption does not mean that carbon gasification proceeds independently of process conditions or that it must always result in the complete removal of deposits. In the analysed flow reactor, carbon remains on the catalyst surface. At the same time, a stream of CO₂ passes through the bed and may maintain local process conditions that deviate from the equilibrium of the Boudouard reaction. Therefore, the actual progress of regeneration is limited by the reaction rate, local concentrations of CO₂ and CO, temperature, and the thermodynamic conditions resulting from comparing the reaction quotient (Q) with the equilibrium constant ($K_p(T)$). The validity of the assumption $m_C^* = 0$ will be assessed using numerical simulation results for the regeneration process. Furthermore, the carbon deposited on the catalyst during methane reforming with carbon dioxide is produced by one of three chemical reactions:



4. Mathematical model of coke formation in the syngas production reactor

To determine the mass of carbon deposited on the catalyst, a mathematical model describing methane reforming in a fixed-bed flow reactor was used. This model was described in detail

in the work of Lewak (2025). A one-dimensional fixed-bed reactor model was applied to analyse the influence of reactor wall temperature and total pressure on the course of dry reforming of methane and on the amount of carbon deposited on the catalyst. The geometric parameters describing the bed and reactor are listed in the table below (see Table 1).

Table 1. Fixed-bed reactor process parameters

D_w [mm]	L [mm]	d_p [mm]	ε [–]
21.6	630	9	0.5

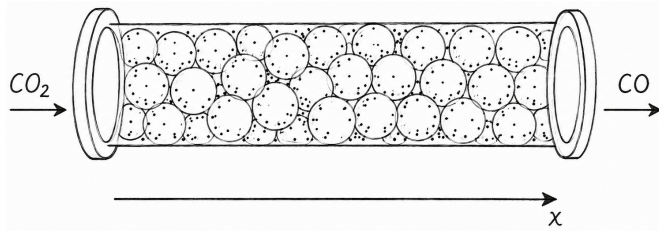


Figure 1. Schematic diagram of a horizontal packed-bed reactor with spherical catalyst particles and deposited carbon.

The reactor scheme for syngas production and catalyst regeneration is shown in Fig. 1. Owing to the conditions under which the gas-phase reforming reaction is carried out at temperatures above 500 °C, the reforming process is modelled using mass balances of the reactants and the gas enthalpy along the reactor. The reactor consists of a horizontal tube filled with catalyst particles of uniform shape (spheres with diameter d_p). The catalyst is nickel oxide supported on Al_2O_3 . Before the reforming reaction, nickel oxide must be reduced to nickel, which catalyses both methane reforming and undesirable reactions (see Eqs. (18)–(21)). The simulation of reactor operation during the reforming step was discussed in detail in the work of Lewak (see Lewak, 2025). In the present work, the mathematical model of the syngas production reactor was used to determine the operating time of the reforming step, t_{DRM} . The mathematical model (see Eqs. (7) and (8)) incorporates the kinetic model of methane reforming and the undesirable reactions. The kinetic reaction model was developed experimentally by Cherbański and co-workers (Cherbański et al., 2021).

$$\varepsilon \frac{d\dot{n}_i}{dx} = \sum_{j=1}^N \nu_{ij} R_j \rho_{\text{cat}} (1 - \varepsilon) F \quad (7)$$

$$\varepsilon \frac{dh}{dx} = \sum_{j=1}^N (-\Delta H_j) R_j \rho_{\text{cat}} (1 - \varepsilon) F + U_w \pi d_w (T - T_w) \quad (8)$$

where $i = \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2, \text{H}_2\text{O}$. Using the mathematical model (see Eqs. (7)–(8)), it is possible to determine the mass flux of carbon deposited on the catalyst along the reactor during one operating cycle. Fig. 2 shows the distribution of the carbon deposition rate on the catalyst during dry reforming of methane.

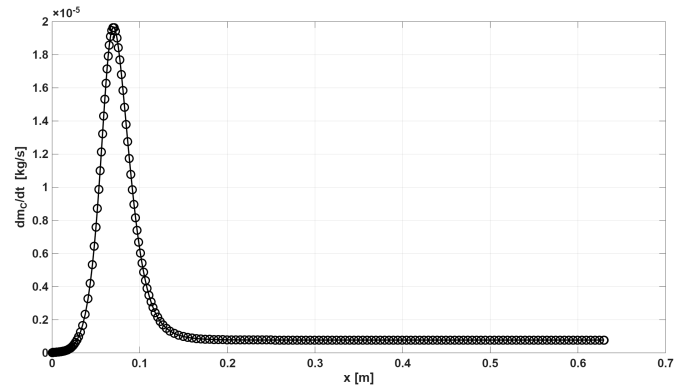


Figure 2. Axial distribution of the carbon deposition rate on the catalyst during DRM9 at $\dot{n}_{\text{CO}_2} = \dot{n}_{\text{CH}_4} = 0.5$ mol/min, $T_{\text{wall}} = T_{\text{DRM}} = 1223$ K, $P = 101325$ Pa, $\bar{\tau}_p = 0.743$ s.

During one reactor operating cycle in the methane reforming step (the mean gas residence time in the reactor), the following mass of carbon is deposited on the catalyst:

$$m_{\text{carbon}}^{\text{cycle}}(\bar{\tau}_p) = \sum_i^n \frac{dm_C(x_0 + i\Delta x_i)}{dt} \bar{\tau}_p \quad (9)$$

5. Methodology for determining the operating time of the DRM stage before regeneration

The duration of the dry reforming of methane step before the start of catalyst regeneration, denoted as t_{DRM} , was selected based on the maximum allowable amount of carbon deposited on the catalyst. It was assumed that the carbon deposit may cover only a small fraction of the catalyst's external surface, so it does not significantly affect the bed porosity ε , the gas flow velocity, or the rate of the reforming process. The coefficient α described the allowable degree of catalyst surface coverage by carbon, defined as the ratio of the catalyst surface covered with carbon, F_{carbon} , to the total catalyst surface, F_{cat} :

$$\alpha = \frac{F_{\text{carbon}}}{F_{\text{cat}}} \quad (10)$$

Using the above relationship, the catalyst surface occupied by carbon can be determined from:

$$F_{\text{carbon}} = \alpha F_{\text{cat}} = \alpha \frac{6}{d_p} (1 - \varepsilon) FL \quad (11)$$

To quantify the total mass of carbon deposited on the catalyst, it was assumed that the carbon forms prismatic structures on the surface of the spherical catalyst particles, whose total volume can be determined by specifying the maximum thickness of such a layer, δ_{carbon} :

$$V_{\text{carbon}}^{\text{total}} = F_{\text{carbon}} \delta_{\text{carbon}} = \alpha \frac{6}{d_p} (1 - \varepsilon) FL \delta_{\text{carbon}} \quad (12)$$

$$m_{\text{carbon}}^{\text{total}} = \rho_{\text{carbon}} V_{\text{carbon}}^{\text{total}} \quad (13)$$

In the calculations, the effective density of the carbon deposit was assumed to be 1800 kg/m^3 . This value corresponds to a density typical of partially ordered carbon materials, such as carbon black and carbon fibres, and was adopted as a model parameter. The number of reactor operating cycles during methane reforming, N_{cycles} , was determined from the ratio of the total carbon mass to the mass of carbon deposited on the catalyst during one cycle:

$$N_{\text{cycles}} = \text{round} \left(\frac{m_{\text{carbon}}^{\text{total}}}{m_{\text{carbon}}^{\text{cycle}}} \right) \quad (14)$$

The reactor operating time during one reforming cycle was calculated using the following relationship:

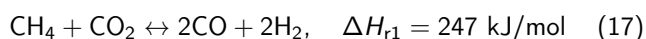
$$t_{\text{DRM}} = N_{\text{cycles}} \bar{\tau}_p \quad (15)$$

The carbon deposition rate determined from the DRM model, denoted as dm_C/dt , was treated as the local rate of carbon deposit growth along the reactor axis. To determine the amount of carbon deposited on the catalyst after a specified reactor operating time, this rate was multiplied by the duration of the reforming step, t_{DRM} .

This gives the function:

$$m_{C,\text{DRM}}(x_j, t_{\text{DRM}}) = m_{C0}(x_j) = \frac{dm_C}{dt}(x_j) t_{\text{DRM}} \quad (16)$$

Dry reforming of methane is the reaction between methane and carbon dioxide:



In addition to this reaction, undesirable reactions also occur in the reactor:



Three conclusions follow from the numerical simulations performed using the mathematical model describing dry reforming of methane together with the accompanying reactions (see Eqs. (7)–(8)). The first conclusion concerns the reaction operating conditions. Strongly endothermic reactions require operation at high temperatures. The temperature limitation is the thermal stability of the catalyst. As shown by the simulation results, because all chemical reactions are reversible, the reaction process is more favourably operated at lower pressure. The limitation is related to safety considerations when working with highly flammable gases. Therefore, the regeneration process is proposed to be carried out at $P = 101325 \text{ Pa}$. The second conclusion is shown in Table 2. Above a certain wall temperature, a further increase in T_{wall} favours an extension of the reactor operating time by reducing the amount of carbon deposited during one operating cycle (see $m_{\text{carbon}}^{\text{cycle}}$ in Table 2). Table 2 summarises the calculated operating parameters of the reforming step. As can be seen, from a wall temperature of $T_{\text{wall}} = 923 \text{ K}$, a further increase in wall temperature causes a decrease in the total mass of carbon deposited during one operating cycle. As a result, the total duration of the reforming step is extended (see the increase in t_{DRM} in Table 2). The third conclusion is unfavourable, because the total duration of the reforming step is very short; therefore, for the entire process to be economically viable, it should be carried out in a cascade of tubular reactors.

Interestingly, the increase in methane and carbon dioxide conversion in the lower temperature range is accompanied by an increase in the total mass of carbon deposited on the catalyst. This means that the carbon deposited on the catalyst originates primarily from methane decomposition rather than from the other two reactions. The second conclusion from the numerical simulations of the reactor during the reforming step is that operation at higher temperatures extends the reactor operating time.

Table 2. Summary of reactor operating parameters during dry methane reforming, $\alpha = 0.1$, $\delta_{\text{carbon}} = 2 \text{ mm}$, $m_{\text{carbon}}^{\text{total}} = 26.3 \text{ g}$, $\dot{n}_{\text{CO}_2} = \dot{n}_{\text{CH}_4} = 0.5 \text{ mol/min}$, $P = 101325 \text{ Pa}$.

Name	$T_{\text{DRM}} [\text{K}]$	$\bar{\tau}_p [\text{s}]$	$m_{\text{carbon}}^{\text{cycle}} [\text{g}]$	$N_{\text{cycles}} [-]$	$t_{\text{DRM}} [\text{s}]$	$\alpha_{\text{CH}_4}^{\text{outlet}} [-]$	$\alpha_{\text{CO}_2}^{\text{outlet}} [-]$
DRM1	823	0.58	0.576	46	26.55	0.31	0.35
DRM2	873	0.67	2.178	12	8.06	0.60	0.47
DRM3	923	0.78	4.181	6	4.67	0.80	0.57
DRM4	973	0.83	3.821	7	5.79	0.87	0.71
DRM5	1023	0.87	2.674	10	8.71	0.91	0.84
DRM6	1073	0.91	1.693	16	14.56	0.94	0.92
DRM7	1123	0.95	1.091	24	22.88	0.96	0.96
DRM8	1173	1.00	0.785	34	33.93	0.97	0.98
DRM9	1223	1.04	0.606	43	44.65	0.98	0.99
DRM10	1273	1.07	0.496	53	56.92	0.99	1.00

6. Mathematical model of catalyst regeneration

The syngas production process in the dry reforming of methane step can be described by a mathematical model under steady-state conditions. In such a case, the main objective of the calculations is to determine the distributions of reactant concentrations, temperature and carbon deposit formation rate along the reactor under fixed operating conditions. This approach is justified when a single reactor operating step in syngas production mode is analysed, and the amount of deposited carbon is treated as the result of a mass balance for a fixed residence time of the reactants in the bed. The catalyst regeneration step, however, is transient. After the DRM step, a non-uniform distribution of carbon mass is deposited on the catalyst along the bed, forming the initial condition for the regeneration process. Therefore, the regeneration model must describe changes in CO_2 and CO concentrations in the gas phase, as well as changes in the local carbon mass $m_C(x, t, T, P)$, simultaneously as functions of axial position x and regeneration time t . Thus, in contrast to the syngas production model, the regeneration model requires solving a system of transient equations describing convective transport of the reactants and carbon dioxide-mediated carbon gasification.

Catalyst regeneration was described by the reverse Boudouard reaction (see Eq. (21)). This reaction removes carbon deposited on the catalyst and simultaneously forms carbon monoxide. It is an endothermic process, and its progression towards CO formation is favourable mainly at high temperatures. Alsawadi and co-workers indicate that the reverse Boudouard reaction usually requires temperatures above 700°C for the chemical equilibrium to shift towards CO production (Alsawadi et al., 2025). Similarly, in the studies by Mianowski and co-workers, the Boudouard-Bell reaction was analysed at high temperatures (800 , 850 , and 900°C) under elevated pressure, confirming the importance of temperature and pressure in assessing the reactivity of carbon materials towards CO_2 (Mianowski et al., 2012). In simulations of the catalyst regeneration cycle, the empirical equation describing the equilibrium constant of the reversible reaction presented by Mianowski and co-workers was used.

The model assumes that the carbon gasification reaction can occur only when the local gas composition satisfies the thermodynamic condition resulting from the equilibrium constant of the reverse Boudouard reaction. For each reactor discretisation element, a local reaction quotient is defined:

$$Q(x, t) = \frac{p_{\text{CO}}^2(x, t)}{p_{\text{CO}_2}(x, t)} \quad (22)$$

This quotient makes it possible to determine at each integration step whether the following condition is satisfied:

$$Q(x, t) < K_p(T) \quad (23)$$

Accordingly, the parameter $\Phi(x, t)$ was introduced to set the reaction term to zero when equilibrium of the reverse Boudouard reaction is reached in the reactor:

For $Q(x, t) < K_p(T)$

$$\Phi(x, t) = 1 \quad (24)$$

For $Q(x, t) \geq K_p(T)$

$$\Phi(x, t) = 0 \quad (25)$$

The proposed mathematical model of the catalyst regeneration process is valid under the following simplifying assumptions:

- The catalyst regeneration process is carried out under isothermal conditions.
- Regeneration is carried out at a sufficiently high molar flow rate of carbon dioxide; therefore, reactant transport along the reactor is dominated by convection and the effect of molecular diffusion can be neglected.
- The gasification of carbon deposited on the catalyst can be described by a first-order kinetic model adapted from the work of Alsawadi et al. (2025).
- The carbon deposition rate on the catalyst during the DRM step is constant in time and depends only on the position along the reactor axis, according to the distribution determined in the model of Lewak (2025).
- The gas velocity in the reactor depends on the local density of the gas mixture and therefore on the axial coordinate of the reactor.
- The degree of catalyst surface coverage by carbon, denoted as α , is sufficiently small that it does not significantly affect the dry reforming of methane rate.
- The thickness of the carbon layer deposited on the catalyst, denoted as δ_{carbon} , is sufficiently small that it does not significantly change the bed porosity.
- The volume of the carbon deposit is much smaller than the volume of the solid catalyst phase:

$$V_{\text{carbon}} \ll V_{\text{cat}} \quad (26)$$

The mathematical model of the carbon gasification/catalyst regeneration reactor takes the following form:

$$-\frac{d\Delta m_C}{dt} = R_{mC}(x, t, T, P) \quad (27)$$

$$= A_0 e^{-\frac{E}{RT}} \Delta m_C(x_j, t, T, P) \Phi(x, t)$$

$$\frac{\partial C_{\text{CO}_2}}{\partial t} + \frac{\partial}{\partial x}(u C_{\text{CO}_2}) = -\frac{1}{M_C V_{\text{cat}} \epsilon} R_{mC}(x, t, T, P) \quad (28)$$

$$\frac{\partial C_{\text{CO}}}{\partial t} + \frac{\partial}{\partial x}(u C_{\text{CO}}) = \frac{2}{M_C V_{\text{cat}} \epsilon} R_{mC}(x, t, T, P) \quad (29)$$

Since the equations describing the gas mass balances are first-order partial differential equations, whereas the local changes in the mass of carbon deposited on the catalyst are described by a first-order ordinary differential equation, the method of lines is an appropriate method for their solution. For this purpose, the derivative describing the convective gas

term along the reactor was discretised using the following approximation formula:

$$\frac{\partial}{\partial x}(uC_k) \simeq \frac{u(x_j, t)C_k(x_j, t) - u(x_{j-1}, t)C_k(x_{j-1}, t)}{x_j - x_{j-1}} \quad (30)$$

where $k = \text{CO}_2$ and CO .

A first-order upwind finite-difference scheme was used to approximate the first spatial derivative of the convective term. The advantage of this approach is its numerical simplicity and good computational stability, especially for convection-reaction problems in which the dominant transport mechanism is gas flow along the reactor axis. The upwind scheme accounts for the flow direction and therefore limits the formation of nonphysical concentration oscillations that may occur with central or higher-order schemes in convection-dominated problems. This is particularly important in the analysed model because the concentrations of CO_2 and CO , and the mass of deposited carbon, must remain non-negative throughout the calculations.

The disadvantage of the first-order upwind scheme is its relatively high numerical diffusion. This means that sharp concentration gradients along the reactor may be artificially smoothed, especially when the spatial discretisation grid is too coarse. Consequently, the method may lead to a less accurate representation of local changes in gas composition and reaction rate in regions with strong spatial gradients. Nevertheless, the first-order upwind scheme was adopted as the baseline approach because of its stability, numerical robustness and consistency with the direction of convective transport in the tubular reactor.

The carbon distribution obtained from the DRM simulation was used as the initial condition for the catalyst regeneration model. Since the spatial grid used in the regeneration model may differ from the grid used in the DRM calculation, the carbon mass cannot be transferred directly as point values without affecting the total carbon mass in the system. Therefore, the carbon distribution obtained from the DRM stage was first recalculated into the mass of carbon assigned to spatial intervals.

For the DRM grid, the carbon mass contained in a given spatial interval was used to determine the local linear carbon-mass density:

$$q_{m\text{CO}}(x_j) = \frac{\Delta m_{\text{CO}}(x_j)}{x_j - x_{j-1}} \quad (31)$$

The initial mass of carbon assigned to the j -th element (x_j) of the regeneration grid was calculated as:

$$\Delta mC(x_j, 0) = \int_{x_{j-1}}^{x_j} q_{m\text{CO}}(x) dx \quad (32)$$

where x_{j-1} and x_j denote the boundaries of the j -th spatial element in the regeneration model. The discrete values x_0 and mC_0 , obtained from the DRM simulation, were first used to

determine the corresponding discrete values of the local linear carbon-mass density $q_{m\text{CO}}$. The $q_{m\text{CO}}$ values between the grid nodes were then reconstructed using cubic spline interpolation. In the numerical implementation, the integral in Eq. (32) was evaluated numerically over each new regeneration-grid interval. This procedure preserves the non-uniform axial distribution of the carbon deposit while ensuring that the total amount of carbon introduced into the regeneration model is independent of the spatial discretisation used in the regeneration step.

The differential volume of the solid catalyst phase ΔV_{cat} in the reactor can be expressed as:

$$\Delta V_{\text{cat}} = (1 - \varepsilon)\Delta V_{\text{total}} = (1 - \varepsilon)F(x_j - x_{j-1}) \quad (33)$$

In the numerical implementation, the quantity V_{cat} appearing in the source term of the balance equations was determined locally for successive reactor discretisation elements as ΔV_{cat} , according to Eq. (33).

The gasification reaction rate expressed as the number of moles per unit volume of a differential reactor slice can be written as:

$$\frac{1}{MC \cdot \Delta V_{\text{cat}} \cdot \varepsilon} R_{mC}(x, t, T, P) = \frac{1}{MC \cdot (1 - \varepsilon) \cdot F \cdot (x_j - x_{j-1}) \cdot \varepsilon} A_0 e^{-\frac{E}{RT}} \Delta mC(x, t, T, P) \Phi(x, t) \quad (34)$$

The density of the gas mixture at each point of the reactor and at each integration step was determined from the local gas composition, temperature and total pressure. The instantaneous concentrations of CO_2 and CO were used to calculate the local mole fractions of the mixture components. The mean molar mass and compressibility factor Z of the gas mixture were then determined using the Redlich-Kwong equation of state. The gas density was calculated from the modified real-gas equation:

$$\rho_{\text{gas}}(x, t) = \frac{PM_{\text{mix}}(x, t)}{Z(x, t)RT} \quad (35)$$

where P denotes the total pressure, M_{mix} the mean molar mass of the mixture, T the temperature, R the universal gas constant, and Z the compressibility factor of the gas mixture.

Based on the local gas density calculated in this way, the interstitial velocity of the mixture flowing through the catalytic bed was determined. It was assumed that the total mass flow rate of gas fed to the reactor is known, whereas the local velocity varies along the reactor due to changes in mixture composition and density. The interstitial velocity was calculated from the following relationship:

$$u(x, t) = \frac{\dot{m}_{\text{gas}}}{\rho_{\text{gas}}(x, t) \varepsilon F} \quad (36)$$

where $\dot{m}_{\text{gas}}$ is the gas mass flow rate, ε is the bed porosity, and F is the cross-sectional area of the reactor. The velocity determined in this way was then used in the convective term

of the balance equations for CO₂ and CO. The mathematical model of the catalyst regeneration process was solved using Matlab R2025b. The resulting system of ordinary differential equations was integrated using ode15s. The ode15s solver is intended for stiff systems and uses numerical differentiation formulae (NDF) of orders 1–5 with variable step size and variable order. The NDF approach is related to backward differentiation formulae (BDF), also known as Gear methods, which can also be optionally used by the ode15s solver.

7. Numerical simulation results for catalyst regeneration

Before analysing the regeneration results, the influence of spatial grid discretisation should be considered. If the grid is too coarse, the first-order upwind scheme may introduce excessive numerical diffusion, artificially smoothing the concentration and carbon-mass profiles. On the other hand, excessive grid refinement increases the number of ordinary differential equations and the computational cost, and may increase the stiffness of the resulting system.

In the catalyst regeneration model, a non-uniform spatial grid was used, with local refinement linked to the initial distribution of the carbon mass deposited on the catalyst. The highest number of computational points was introduced in the region where the distribution ($m_{C0} = f(x)$), obtained from the DRM-stage simulation, reached its maximum. This approach enables a more accurate representation of the local course of carbon gasification in the part of the reactor where the amount of carbon deposit is highest and where the largest changes in the reaction rate are expected. Local grid refinement in a selected reactor region represents a compromise between numerical accuracy and computational cost. The use of a uniformly very fine grid would lead to a substantial increase in the number of ordinary differential equations obtained after applying the method of lines. In contrast, an excessively coarse grid could fail to correctly represent local changes in reactant concentrations and carbon mass in the region of the highest regeneration activity. Therefore, a non-uniform grid was adopted, refined in the vicinity of the maximum initial mass of deposited carbon. The choice of grid type depended on the nature of the axial carbon deposition profile obtained for each DRM case. For cases DRM1–DRM5, a uniform grid was used because the carbon mass distribution along the reactor did not require additional local refinement of the computational points. In contrast, for cases DRM6–DRM10, a non-uniform grid with adjusted discretisation was applied because the maximum carbon deposition was more localised and required a more accurate representation in the regeneration model. This approach made it possible to limit the number of ordinary differential equations while maintaining higher computational accuracy in the regions important for the course of carbon gasification.

To analyse the effect of the degree of numerical grid discretisation in the x -direction, the parameter N was introduced. The value $N - 1$ defines the number of intervals into which the reactor was divided along its length. A control parameter was also introduced to describe the total mass of carbon contained in the reactor as a function of time:

$$m_{\text{carbon}}^{\text{total}}(t) = \sum_{x=0}^L \Delta m_C(t, x) \quad (37)$$

The second parameter introduced was the degree of carbon gasification, ξ_C , expressed by the following relationship:

$$\xi_C(t) = \frac{m_{\text{carbon}}^{\text{total}}(0) - m_{\text{carbon}}^{\text{total}}(t)}{m_{\text{carbon}}^{\text{total}}(0)} \quad (38)$$

To investigate the effect of the degree of numerical grid discretisation in the x -direction, the highest analysed regeneration temperature, equal to 1270 K, was selected. This value was selected as a high-temperature operating point close to the upper range commonly considered for methane reforming over nickel-based catalysts. The choice of this temperature makes it possible to perform the analysis under the most demanding conditions for the carbon gasification rate. According to the Arrhenius relationship, an increase in temperature leads to a significant increase in the reaction rate; therefore, at 1270 K, removal of the carbon deposit proceeds much faster than at lower temperatures. Under such conditions, local changes in carbon mass and reactant concentrations may be more dynamic, which increases the requirements imposed on the adopted numerical grid. An insufficient number of axial intervals may then lead to an inaccurate representation of local changes in the reaction rate and in the carbon-mass profile.

The analysis performed at the highest temperature, therefore, represents the most sensitive test for possible errors resulting from insufficient spatial discretisation. If the numerical solution remains stable and satisfies the mass-balance requirements at 1270 K, the adopted discretisation approach is also

Table 3. Summary of the effect of numerical grid discretisation on the key parameters describing carbon gasification, DRM8 $\dot{n}_{\text{CO}_2} = 1$ mol/min, $\dot{n}_{\text{CO}} = 0$ mol/min, $P = 101325$ Pa, $T_{\text{reg}} = 1270$ K, $t_{\text{reg}} = 3600$ s.

N [–]	$m_{\text{carbon}}^{\text{total}}(0)$ [kg]	$m_{\text{carbon}}^{\text{total}}(t_{\text{reg}})$ [kg]	$\xi_C(t_{\text{reg}})$ [–]
64	0.026689	0.009286	0.65207
71	0.026689	0.009286	0.65207
79	0.026689	0.009286	0.65207
91	0.026689	0.009286	0.65207
106	0.026689	0.009286	0.65207
127	0.026689	0.009286	0.65207
158	0.026689	0.009286	0.65207
211	0.026689	0.009286	0.65207
316	0.026689	0.009286	0.65207
631	0.026702	0.009291	0.65207

suitable for lower regeneration temperatures. Table 3 summarises the total mass of carbon deposited on the catalyst at the beginning and end of the regeneration process, i.e., after one hour of system operation. As can be seen, the influence of discretisation becomes noticeable for values above $N = 316$. Therefore, a discretisation degree of $N = 211$ was selected for further simulations as a compromise between adequate spatial discretisation and the total time required to obtain the numerical solution. On this basis, $N = 211$ was adopted in the subsequent regeneration simulations unless stated otherwise.

The kinetic model of carbon gasification is based on first-order kinetics, while the parameters in the Arrhenius equation reported by Alsawadi et al. (2025) indicate a very slow gasification reaction. Therefore, the catalyst regeneration time, t_{reg} , must be sufficiently long to allow a reasonable degree of carbon conversion and, consequently, effective catalyst regeneration. At the same time, t_{reg} must not be excessively long, because as the mass of carbon deposited on the catalyst decreases, the gasification rate decreases substantially. Moreover, excessively long regeneration times are associated with high operating costs of the installation. For this reason, a regeneration time of $t_{\text{reg}} = 3600$ s was adopted in the simulations.

Before presenting the comparative analysis for all DRM cases and regeneration temperatures, the behaviour of the regeneration model is first illustrated using case DRM10 at a regeneration temperature of 1200 K. This case was selected as an example to demonstrate the characteristic changes in CO_2 concentration, CO concentration and deposited carbon mass during the transient regeneration step. The purpose of this example is not to identify the optimal regeneration conditions, but to show how the proposed mathematical model describes the local evolution of the gas phase and carbon deposit in the fixed-bed reactor. The simulation of reactor operation during the catalyst regeneration cycle was based on the amount of carbon deposited during the methane reforming cycle. For this purpose, the data presented in Table 2 were used, and the system of equations describing methane reforming was

solved numerically (see Eqs. (7)–(8)). Simulations of the regeneration step were performed at seventeen temperatures: 973 K, 1000 K, 1030 K, 1050 K, 1070 K, 1100 K, 1130 K, 1150 K, 1180 K, 1190 K, 1200 K, 1210 K, 1220 K, 1230 K, 1240 K, 1250 K, and 1270 K. The steady-state DRM model was solved using the ode23s function in Matlab R2025b, because the system describing methane reforming is stiff. The transient catalyst regeneration model, formulated using the method of lines, resulted in a larger stiff system of ordinary differential equations and was therefore integrated with the ode15s solver. The total catalyst regeneration time was selected as 3600 s. This time horizon was chosen to enable analysis of the transient regeneration process over a sufficiently long period relative to the characteristic rate of carbon gasification. It also allows the gradual decrease in the local carbon mass along the reactor to be observed without imposing complete regeneration a priori. A regeneration time of 3600 s provides a convenient basis for comparing operating temperatures under identical simulation conditions. Therefore, this value was treated as a fixed process time for assessing the effectiveness of CO_2 -assisted catalyst regeneration.

The distribution of carbon dioxide concentration along the reactor and over time indicates that, during regeneration, the C_{CO_2} concentration remains practically constant throughout the entire bed volume (see Fig. 3).

The observed change in CO_2 concentration is small compared with the absolute concentration in the gas phase. This means that the amount of CO_2 consumed in the carbon gasification reaction is small relative to the amount of CO_2 flowing through the reactor. This is consistent with the assumption that regeneration is carried out at a sufficiently high carbon dioxide flow rate to maintain process conditions away from the equilibrium state of the reverse Boudouard reaction. The largest local changes in CO_2 concentration occur near the final section of the bed, where the initial mass of deposited carbon is the highest. In this part of the reactor, the carbon gasification rate is the highest; therefore, local CO_2 consumption is

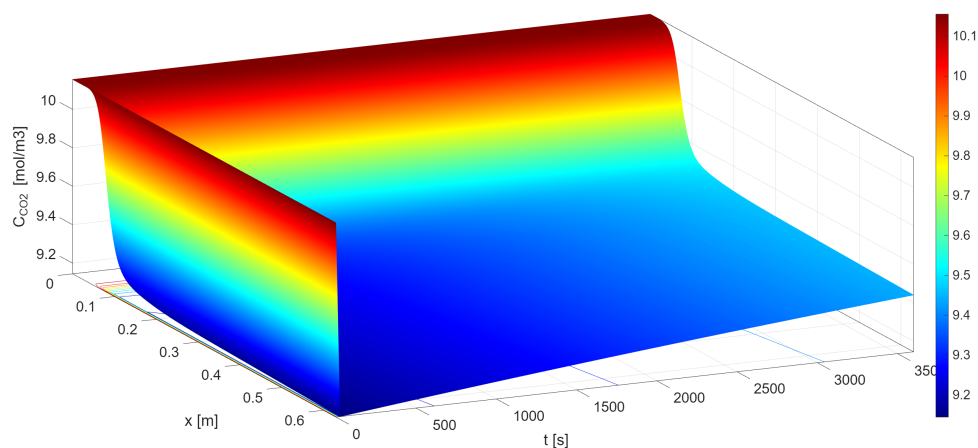


Figure 3. Distribution of C_{CO_2} concentration along the reactor as a function of catalyst regeneration time DRM10, $\dot{n}_{\text{CO}_2} = 1$ mol/min, $\dot{n}_{\text{CO}} = 0$ mol/min, $P = 101325$ Pa, $T_{\text{reg}} = 1200$ K.

most clearly visible. Nevertheless, the decrease in CO_2 concentration remains very small, indicating that the regeneration step is not limited by the availability of carbon dioxide in the gas phase but is primarily governed by gasification kinetics and the local amount of available carbon deposit. The distribution of C_{CO} as a function of axial position and regeneration time indicates that the changes in CO concentration remain relatively small during the analysed regeneration step. This suggests that the extent of carbon gasification is limited and that the heat associated with CO formation is insufficient to significantly alter the assumed isothermal character of the process.

Therefore, the adoption of an isothermal regeneration model is justified under the present simulation conditions. Moreover, the low CO concentration maintained in the gas phase indicates that the reaction system remains far from the equilibrium state of the reverse Boudouard reaction. Under these conditions, the reaction quotient Q remains well below the equilib-

rium constant $K_p(T)$, thereby preserving the thermodynamic driving force for carbon gasification. This confirms that, in the analysed case, the regeneration process is controlled mainly by the gasification kinetics and the local amount of deposited carbon, rather than by equilibrium limitations. Figure 5 presents the changes in the mass of carbon deposited on the catalyst as a function of axial position along the reactor and regeneration time. The distribution of the carbon mass, $(\Delta m_C(t, x))$, shows that the amount of carbon deposited on the catalyst gradually decreases during regeneration. The carbon loss is most clearly visible in the regions where the deposit's initial mass was highest. At the same time, in the initial section of the reactor, the carbon mass is already low at the beginning of regeneration; therefore, the changes in this region are limited. The resulting distribution confirms that the regeneration process is spatially non-uniform and directly depends on the axial distribution of carbon formed during the DRM step.

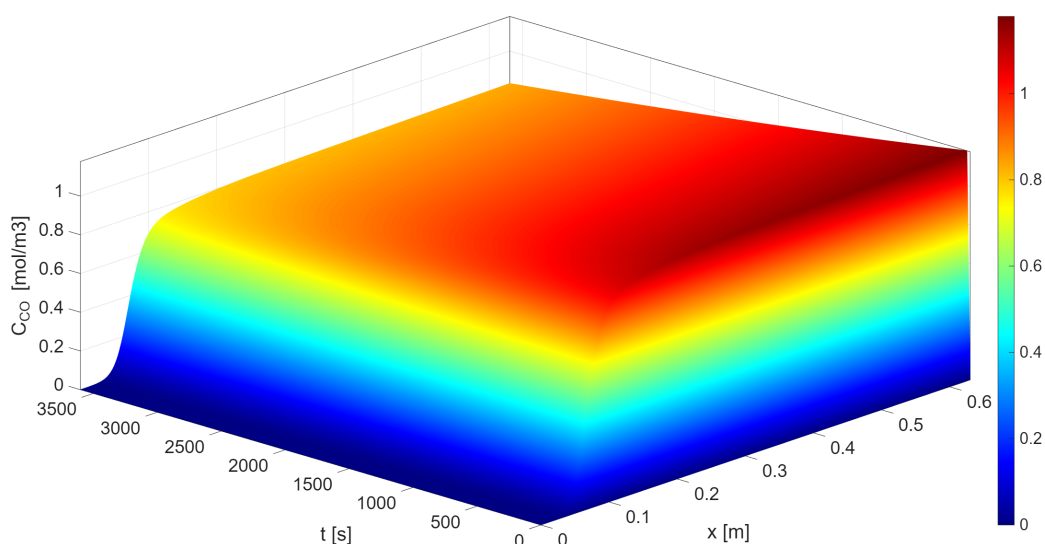


Figure 4. Distribution of C_{CO} concentration along the reactor as a function of catalyst regeneration time, DRM10, $\dot{n}_{\text{CO}_2} = 1 \text{ mol/min}$, $\dot{n}_{\text{CO}} = 0 \text{ mol/min}$, $P = 101325 \text{ Pa}$, $T_{\text{reg}} = 1200 \text{ K}$.

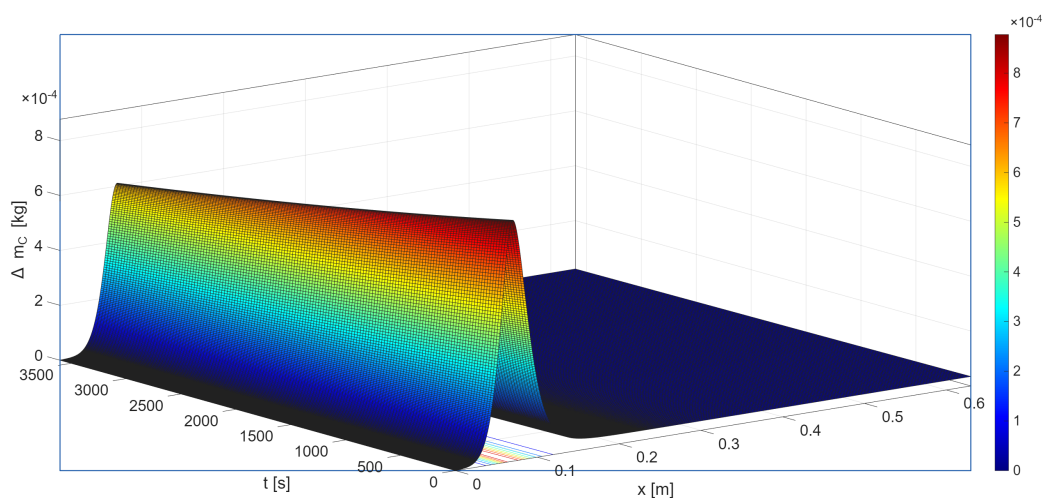


Figure 5. Distribution of the deposited carbon mass, $\Delta m_C(t, x)$, along the reactor as a function of catalyst regeneration time, DRM10, $\dot{n}_{\text{CO}_2} = 1 \text{ mol/min}$, $\dot{n}_{\text{CO}} = 0 \text{ mol/min}$, $P = 101325 \text{ Pa}$, $T_{\text{reg}} = 1200 \text{ K}$.

As time progresses, the surface representing the carbon mass decreases, indicating the progressive removal of the carbon deposit from the catalyst. No rapid or instantaneous disappearance of carbon throughout the entire bed is observed; instead, its mass decreases gradually. This behaviour is consistent with the first-order kinetic model used in this work, in which the gasification rate is proportional to the current amount of carbon available in a given catalyst volume element. As the local carbon mass decreases, the rate of its further removal also decreases. The results obtained at 1200 K indicate that the assumption ($m_C^* = 0$) has process-related validity in the analysed regeneration model. The deposited carbon can be gradually removed in a CO_2 stream, and its decrease results from the progress of the reverse Boudouard reaction. At the same time, the model does not impose an immediate or artificial removal of the entire deposit, because the regeneration rate is limited by the local carbon mass, temperature, reactant concentrations and the thermodynamic condition associated with the comparison of the reaction quotient (Q) with the equilibrium constant ($K_p(T)$). In summary, the simulation of case DRM10 at a regeneration temperature of 1200 K shows that the regeneration step leads to a gradual decrease in the amount of carbon deposited on the catalyst, with only small CO_2 consumption relative to the amount flowing through the reactor. The obtained results confirm that the proposed model enables the local course of catalyst regeneration to be followed and can be used to assess the time required to remove the carbon deposit after the dry reforming of methane step.

To quantitatively analyse the effect of the catalyst regeneration process, two additional process parameters were introduced. The first parameter, R_{cycle} , defines the ratio of the regeneration time, t_{reg} , to the DRM process time, t_{DRM} :

$$R_{\text{cycle}}(t_{\text{DRM}}, t_{\text{reg}}) = \frac{t_{\text{reg}}}{t_{\text{DRM}}} \quad (39)$$

The parameter R_{cycle} indicates the potential industrial applicability of the regeneration process. Ideally, its value should

be much lower than unity; however, the kinetic model of the gasification process clearly indicates that values close to unity would already represent a significant achievement. In most industrial processes, the value of R_{cycle} will be greater than unity.

The second parameter, I_C , combines the cyclicity of both processes with the degree of carbon gasification, according to the following relationship:

$$I_C(t_{\text{DRM}}, t_{\text{reg}}) = \frac{t_{\text{DRM}}}{t_{\text{reg}}} \xi_C(t_{\text{reg}}) \quad (40)$$

To summarise this part of the study, five process parameters were used to assess the catalyst regeneration process, characterising both the reforming cycle and the catalyst regeneration cycle: $\alpha_{\text{CH}_4}^{\text{outlet}}$ (methane conversion at the reactor outlet), $\alpha_{\text{CO}_2}^{\text{outlet}}$ (carbon dioxide conversion at the reactor outlet), ξ_C (fraction of carbon removed during regeneration), R_{cycle} (ratio of catalyst-regeneration to reforming time), and I_C (indicator of catalyst regeneration efficiency). Analysis of catalyst regeneration after two extreme methane-reforming cases, DRM3 and DRM9, reveals the main advantages and limitations of conducting the process in reforming/regeneration cycles. Figure 6 presents the cumulative distribution of carbon mass along the reactor as a function of catalyst-regeneration time after the methane-reforming stage. Dry reforming of methane was carried out at a wall temperature of $T_{\text{DRM}} = 923$ K (see Table 2, DRM3 case). At such a low temperature, methane reforming with carbon dioxide leads to the rapid accumulation of carbon on the catalyst, as evidenced by the reforming time $t_{\text{DRM}} = 4.67$ s. Consequently, the R_{cycle} parameter is 770.88, which clearly indicates the main obstacle to applying regeneration under industrial conditions. The catalyst regeneration time exceeds the methane reforming time by several hundredfold. The I_C parameter for catalyst regeneration after the DRM3 process is 0.00113; therefore, it remains far from values that would allow the industrial application of the process under these conditions.

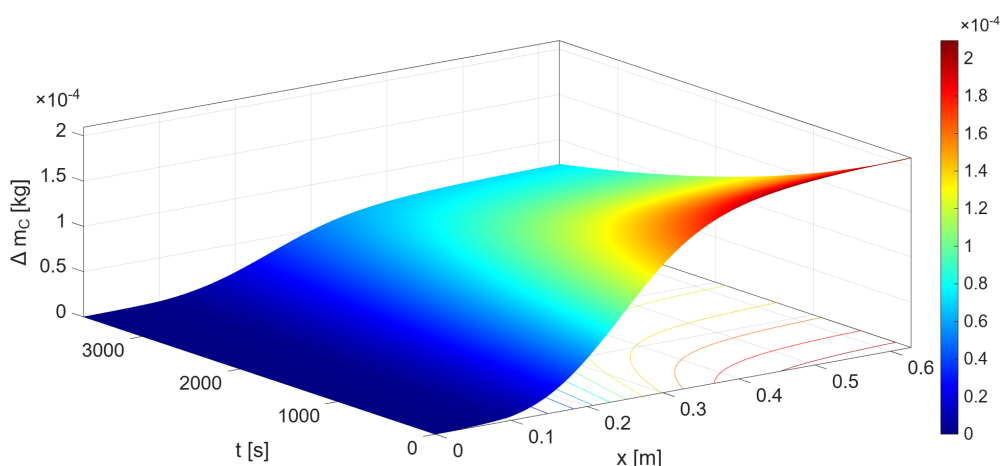


Figure 6. Distribution of the deposited carbon mass, $\Delta m_C(t, x)$, along the reactor as a function of catalyst regeneration time, DRM3, $\dot{n}_{\text{CO}_2} = 1$ mol/min, $\dot{n}_{\text{CO}} = 0$ mol/min, $P = 101325$ Pa, $T_{\text{reg}} = 1270$ K.

In turn, the analysis of regeneration of the catalyst after the reforming process, performed at a reactor wall temperature of $T_{\text{DRM}} = 1223$ K, shows a different curve profile. Conducting dry reforming of methane at high temperature promotes the decomposition reactions of both methane and carbon dioxide, while simultaneously resulting in a much lower rate of carbon deposition on the catalyst than in the previous case. As a result, the time required for catalyst saturation is considerably longer than in the preceding process, with $t_{\text{DRM}} = 44.65$ s. Figure 7 shows the cumulative distribution of carbon mass along the reactor and over time. Carbon gasification proceeds with increasing regeneration time. The value of the R_{cycle} parameter is 80.63, which is approximately seven times lower than that obtained for catalyst regeneration after the DRM3 reforming process. This clearly indicates that both the reforming and regeneration processes should be conducted at the highest possible temperature. The temperature limitation is dictated by technical and safety considerations. The value of the I_C parameter is 0.0079, which is also far from values suitable for industrial applications.

Although the catalyst-regeneration process proceeds locally within the reactor at different rates, the overall degree of carbon gasification is 0.6521 in both cases. This is related to the process conditions. Firstly, at the onset of regeneration, both processes have the same total mass of carbon deposited on the catalyst. Secondly, both processes are carried out under isothermal conditions at the same regeneration temperature, $T_{\text{reg}} = 1270$ K. Therefore, under the fixed regeneration time, initial total carbon mass and gas-flow conditions analysed in this work, the overall degree of carbon conversion, $\xi_C(t_{\text{reg}})$, is governed mainly by the regeneration temperature. Figure 8 shows the effect of regeneration temperature on the degree of carbon conversion, $\xi_C(t_{\text{reg}})$. This comparison indicates that the degree of carbon conversion is related to the regeneration temperature. The higher the regeneration temperature, the higher the degree of carbon conversion. In addition, higher methane-reforming temperatures result in longer reforming-cycle times (see Table 2). The DRM1 case is an exception, for which the reforming cycle time is comparable to those of DRM8, DRM9, and DRM10; however, this is due to the

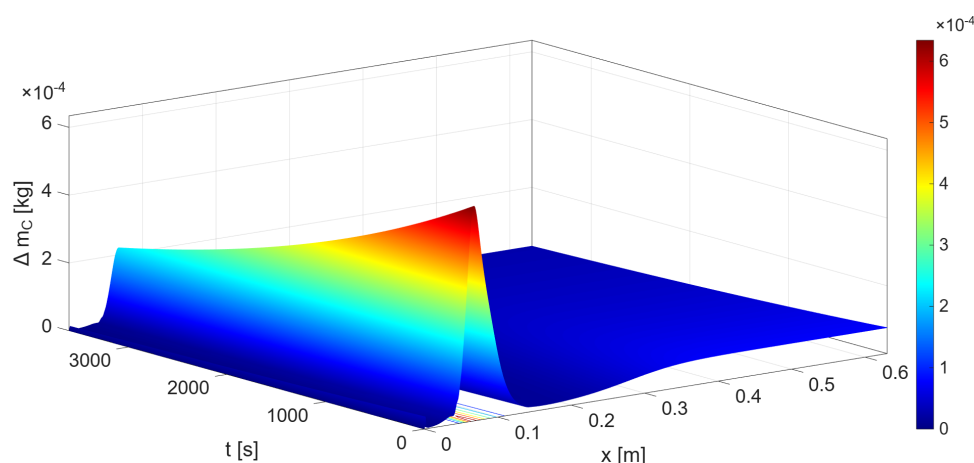


Figure 7. Distribution of the deposited carbon mass, $\Delta m_C(t, x)$, along the reactor as a function of catalyst regeneration time, DRM9, $\dot{n}_{\text{CO}_2} = 1$ mol/min, $\dot{n}_{\text{CO}} = 0$ mol/min, $P = 101325$ Pa, $T_{\text{reg}} = 1270$ K.

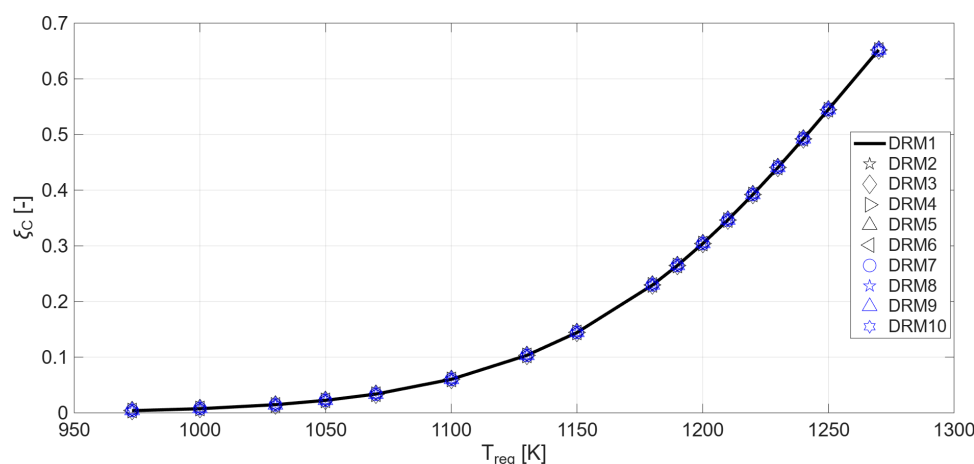


Figure 8. Effect of regeneration temperature on the degree of gasification of carbon deposited on the catalyst, $\dot{n}_{\text{CO}_2} = 1$ mol/min, $\dot{n}_{\text{CO}} = 0$ mol/min, $P = 101325$ Pa.

very low degrees of conversion of methane and carbon dioxide. Nevertheless, the reforming cycles across all ten processes are short, not exceeding 1 minute.

Figure 8 also supports the numerical consistency of the simulations and indicates that the first-order upwind scheme used to discretise the convective term is sufficient under the analysed conditions. This is an important conclusion because higher-order schemes would increase computational cost without altering the main trends observed in the degree of carbon gasification. Figure 9 presents the effect of catalyst regeneration temperature on the I_C parameter for 10 dry methane reforming cases (DRM1–DRM10). The I_C parameter combines the effectiveness of carbon gasification during regeneration with the duration of the reforming/regeneration cycle. Therefore, it can be treated as an indicator of the practical usefulness of cyclic catalyst operation. Higher I_C values indicate more favourable regeneration conditions, i.e., a greater degree of carbon removal relative to the time required for catalyst regeneration.

The results clearly show that the I_C parameter increases with increasing regeneration temperature. This trend is observed for all analysed reforming cases and confirms the strong temperature dependence of carbon gasification with carbon dioxide. At low regeneration temperatures, below approximately 1100 K, the I_C values are very small across all cases, indicating that catalyst regeneration proceeds too slowly to be practically effective. A more pronounced increase in I_C is observed above 1150 K, whereas the highest values are obtained in the temperature range of 1230 – 1270 K. This confirms that high-temperature regeneration is necessary to obtain a meaningful degree of carbon removal within the assumed regeneration time.

The highest I_C values are obtained for the DRM10, DRM1, and DRM9 cases. For DRM10, the increase in I_C with temperature is particularly strong, indicating the most favourable combination of reforming-cycle duration and carbon gasification efficiency. The DRM9 case also shows high I_C values,

especially at elevated regeneration temperatures, suggesting that reforming at high temperatures yields a carbon-deposition profile that can be regenerated more effectively in a cyclic reforming/regeneration process. An apparent anomaly is observed for the DRM1 case. Although this process does not correspond to the most favourable reforming conditions for methane and carbon dioxide conversion, it yields relatively high I_C values. This behaviour results from the very low degree of conversion of methane and carbon dioxide during DRM1. Because the reactants are converted only to a limited extent, the rate of carbon deposition on the catalyst is also relatively low. Consequently, the time required to reach the assumed carbon-loading criterion is longer than in several other reforming cases. Since the I_C parameter includes the effect of the reforming-cycle duration, a longer reforming time artificially increases its value. Therefore, the high I_C value for DRM1 should not be interpreted as evidence of industrial attractiveness, but rather as a consequence of poor reforming performance and slow catalyst carbon loading. For the remaining cases, particularly DRM2–DRM6, the I_C values are considerably lower over the entire temperature range. This indicates that despite increasing the regeneration temperature, the relationship between reforming duration and carbon removal remains unfavourable. In these cases, the regeneration process is not sufficiently efficient given the short reforming cycle time. This observation confirms that the regeneration temperature alone is not the only factor determining the usefulness of cyclic operation. The reforming conditions, the rate of carbon accumulation, the spatial distribution of deposited carbon and the resulting cycle duration must also be considered. Overall, the results indicate that increasing the catalyst regeneration temperature improves the I_C parameter, thereby enhancing the effectiveness of the reforming/regeneration cycle. However, even in the most favourable cases, the I_C values remain below 0.01, indicating that the process is still far from conditions that would be fully attractive for industrial application. The analysis suggests that both stages of the process should be conducted at the highest technically and safely acceptable temperature. At the same time, the inter-

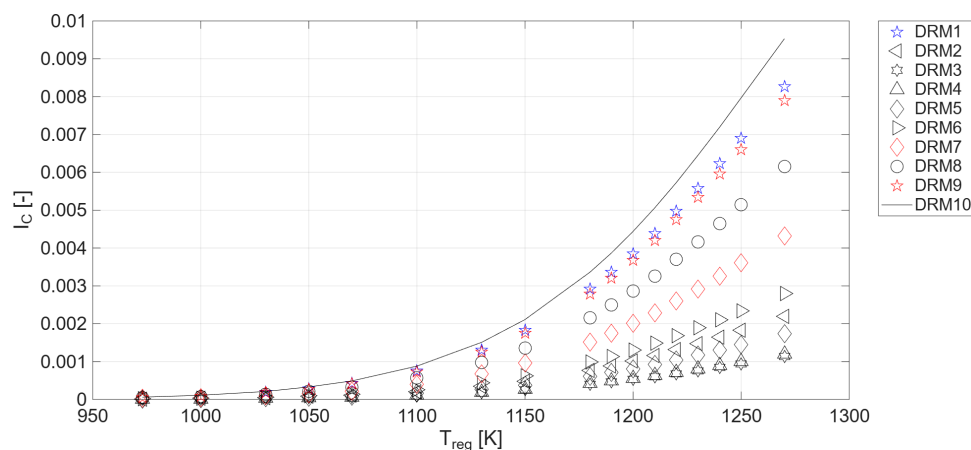


Figure 9. Effect of catalyst-regeneration temperature on the value of the I_C parameter, $\dot{n}_{CO_2} = 1$ mol/min, $\dot{n}_{CO} = 0$ mol/min, $P = 101325$ Pa.

pretation of I_C must be supported by the actual methane and carbon dioxide conversion achieved during reforming, because a high value of this parameter may, in specific cases such as DRM1, result from low reactant conversion rather than from genuinely favourable process performance.

The last of the analysed process parameters is R_{cycle} , which represents the ratio of the catalyst regeneration time to the reforming cycle duration. This parameter is as important as the other four parameters considered in this study. Unfortunately, its appropriate selection in the reforming/regeneration process is difficult, because it depends on many process-related factors. The catalyst regeneration time is determined by the requirement to achieve a sufficiently high degree of carbon gasification, ξ_C . In this work, the regeneration time was treated as a process variable and was selected so that, at the highest analysed regeneration temperature, $T_{\text{reg}} = 1270$ K, the degree of carbon conversion, ξ_C , exceeded 0.6. From the process perspective, this quantity is an operational variable that can be used to optimise process costs. Another variable affecting the R_{cycle} parameter is the methane reforming time. In this case, the key factors are the furnace temperature at which reforming is carried out ($T_{\text{wall}} = T_{\text{DRM}}$) and the assumed maximum degree of carbon surface coverage on the catalyst. Therefore, in the simulations presented in this work, the R_{cycle} parameter changes with increasing furnace temperature during the methane reforming step. Figure 10 presents the effect of the reactor wall temperature during dry reforming of methane on the R_{cycle} parameter. To facilitate interpretation, the blue points denote cases that did not satisfy the criterion requiring both methane and carbon dioxide conversions at the reactor outlet to be higher than 0.9. In contrast, the red points denote cases in which both methane and carbon dioxide conversions at the reactor outlet exceeded 0.9.

The analysis of the R_{cycle} parameter shows that its lowest value, together with high methane and carbon dioxide conversions at the reactor outlet during the reforming cycle, is achieved

at $T_{\text{DRM}} = 1273$ K. This temperature represents the highest permissible operating temperature for nickel catalysts, as they may undergo irreversible deactivation at approximately 1273 K.

8. CONCLUSIONS

The simulations performed in this work confirmed that dry reforming of methane combined with CO_2 -assisted catalyst regeneration can be analysed as a cyclic reforming/regeneration process in a fixed-bed reactor. The proposed model enables using the carbon distribution obtained after the DRM step as the initial condition for the regeneration step and tracking the local removal of deposited carbon along the reactor. The adopted method of transferring the carbon mass between different spatial grids preserved the total carbon balance and enabled the regeneration model to be analysed independently of the discretisation used in the reforming calculation.

The results obtained for the reforming step show that the most favourable operating conditions were achieved at the highest analysed nominal temperature level, close to $T_{\text{DRM}} \approx 1270$ K. Under these conditions, methane and carbon dioxide conversions at the reactor outlet were the highest, the reforming cycle was the longest, and the amount of syngas produced was the largest among the analysed cases. It should be emphasised, however, that the adopted model of carbon accumulation on the catalyst is a simplified representation used to estimate the total mass of deposited carbon. The assumption that the carbon deposit forms prismatic structures should not be interpreted as a direct description of the microscopic mechanism of coke formation. In this model, the key parameter controlling the allowable carbon loading was the assumed degree of catalyst surface coverage by carbon, set to $\alpha = 0.1$.

The simulations of the regeneration step showed that carbon dioxide can be used not only as a reactant in the DRM process, but also as a regenerant. During regeneration,

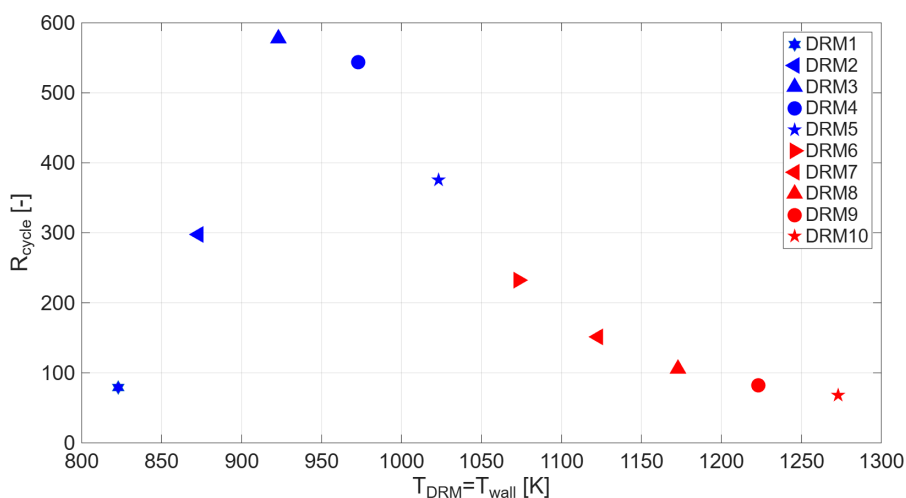


Figure 10. Effect of the DRM wall temperature, T_{DRM} , on the R_{cycle} parameter in dry reforming of methane, $\alpha = 0.1$, $\delta_{\text{carbon}} = 2$ mm, $m_{\text{carbon}}^{\text{total}} = 26.3$ g, $\dot{n}_{\text{CO}_2} = \dot{n}_{\text{CH}_4} = 0.5$ mol/min, $P = 101325$ Pa.

the carbon deposited on the catalyst is gasified to carbon monoxide, a component of syngas. The degree of carbon gasification, ξ_C , increased markedly with regeneration temperature and reached its maximum at $T_{\text{reg}} = 1270$ K. This confirms that high-temperature operation is essential for achieving meaningful carbon removal within the assumed regeneration time of $t_{\text{reg}} = 3600$ s. At the same time, the relatively small changes in CO_2 and CO concentrations during regeneration support the assumption that, under the analysed conditions, the process is controlled mainly by gasification kinetics and by the local amount of deposited carbon rather than by equilibrium limitations.

The analysis of the R_{cycle} and I_C parameters showed that the regeneration step remains the main limitation of the proposed cyclic process. The lowest R_{cycle} values were observed in high-temperature reforming cases, where high conversions of methane and carbon dioxide were also observed. However, even under the most favourable conditions, the regeneration time remained long relative to the reactor's effective operating time during the reforming step. This was reflected in the very low values of the I_C parameter, which combines the degree of carbon gasification with the time relationship between the reforming and regeneration steps. Therefore, increasing I_C , decreasing R_{cycle} , shortening the regeneration time or extending the reforming-cycle duration should be treated as key objectives for further process optimisation.

Despite these limitations, the proposed concept may have practical significance. Effective CO_2 -assisted regeneration could extend catalyst operating time and may enable the use of more active and more stable, but also more expensive, catalytic systems than conventional nickel-based catalysts. Further studies should include experimental verification of the gasification kinetics of the actual carbon deposit formed during DRM, an energy analysis of the entire reforming/regeneration cycle, and optimisation of the regeneration temperature, regeneration time, CO_2 flow rate, and the allowable degree of carbon surface coverage.

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SYMBOLS

A_0	pre-exponential factor in the carbon gasification kinetic equation, s^{-1}
C_i	molar concentration of the i -th component, mol/m^3
C_{CO}	molar concentration of carbon monoxide, mol/m^3
C_{CO_2}	molar concentration of carbon dioxide, mol/m^3
d_p	catalyst particle diameter, m
D_w	reactor inner diameter, m

E_a	activation energy reported for the literature kinetic model, kJ/mol
F	cross-sectional area of the reactor, m^2
F_{carbon}	catalyst surface area covered by carbon, m^2
F_{cat}	total external surface area of the catalyst particles, m^2
h	enthalpy flow rate of the gas mixture, J/s
I_C	comparative cyclic-operation index combining the degree of carbon gasification with the reforming/regeneration time ratio
$K_p(T)$	depending on pressure units equilibrium constant of the reverse Boudouard reaction at temperature T
L	reactor length, m
M_C	molar mass of carbon, kg/mol
M_{mix}	mean molar mass of the gas mixture, kg/mol
m_C	mass of carbon deposited on the catalyst, kg
m_C^*	non-gasifiable carbon mass in the kinetic model, kg
m_{CO}	initial carbon mass distribution obtained from the DRM simulation, kg
$m_{\text{C,DRM}}$	carbon mass distribution after the DRM step, kg
$m_{\text{carbon}}^{\text{cycle}}$	mass of carbon deposited during one reactor operating cycle in the DRM step, kg
$m_{\text{carbon}}^{\text{total}}$	total carbon mass contained in the reactor, kg
$\dot{m}_{\text{gas}}$	gas mass flow rate, kg/s
$\dot{n}_i$	molar flow rate of the i -th component, mol/s
$\dot{n}_{\text{CO}}$	molar flow rate of carbon monoxide at the reactor inlet, mol/min
$\dot{n}_{\text{CO}_2}$	molar flow rate of carbon dioxide at the reactor inlet, mol/min
$\dot{n}_{\text{CH}_4}$	molar flow rate of methane at the reactor inlet, mol/min
N	number of numerical grid points in the axial direction
$N - 1$	number of intervals into which the reactor is divided along its length
N_{cycles}	number of DRM operating cycles before the start of catalyst regeneration
P	total pressure, Pa
P_{total}	total gas pressure, bar or Pa
p_i	partial pressure of the i -th component, bar or Pa
p_{CO}	partial pressure of carbon monoxide, bar or Pa
p_{CO_2}	partial pressure of carbon dioxide, bar or Pa
Q	depending on pressure units reaction quotient of the reverse Boudouard reaction
q_{mCO}	local linear carbon-mass density reconstructed from the DRM carbon distribution, kg/m
R	universal gas constant, $\text{J}/(\text{mol} \cdot \text{K})$
R_{cycle}	regeneration-to-reforming time ratio, defined as $t_{\text{reg}}/t_{\text{DRM}}$
R_j	rate of the j -th chemical reaction, $\text{mol}/(\text{kg} \cdot \text{s})$
R_{mC}	carbon mass gasification rate, kg/s
T	process temperature, K
T_{DRM}	nominal temperature of the dry methane reforming step; in the simulations it corresponds to the reactor wall/furnace temperature used for the DRM stage, K

T_p	gas residence time in the reactor, s
T_{reg}	catalyst regeneration temperature, K
T_{wall}	reactor wall temperature in DRM, K
t	time, s
t_{DRM}	duration of the dry methane reforming step before regeneration, s
t_{end}	final time of the regeneration simulation, s
t_{reg}	catalyst regeneration time, s
U	interstitial gas velocity in the catalytic bed, m/s
U_w	overall heat-transfer coefficient through the reactor wall, W/(m ² · K)
V_{carbon}	volume of the carbon deposit, m ³
V_{cat}	volume of the solid catalyst phase, m ³
V_{total}	total volume of a reactor discretisation element, m ³
x	axial coordinate of the reactor, m
x_0	spatial grid used in the DRM simulation, m
x_j	j -th grid point or boundary of a spatial element, m
x_m	carbon conversion in the kinetic model
y_i	mole fraction of the i -th component
Z	compressibility factor of the gas mixture

Greek symbols:

α	allowable degree of catalyst surface coverage by carbon
$\alpha_{CH_4}^{outlet}$	methane conversion at the reactor outlet
$\alpha_{CO_2}^{outlet}$	carbon dioxide conversion at the reactor outlet
δ_{carbon}	assumed thickness of the carbon layer deposited on the catalyst surface, m
ΔH_j	enthalpy change of the j -th chemical reaction, J/mol
Δm_C	carbon mass assigned to a reactor discretisation element, kg
Δm_{CO}	initial carbon mass assigned to a spatial interval, obtained from the DRM result, kg
ΔV_{cat}	volume of the solid catalyst phase in a discretisation element, m ³
ΔV_{total}	total volume of a reactor discretisation element, m ³
Δx	length of a numerical grid interval in the axial direction, m
ε	bed porosity
ν_{ij}	stoichiometric coefficient of the i -th component in the j -th reaction
ξ_C	degree of carbon gasification
ρ_{carbon}	effective density of the carbon deposit, kg/m ³
ρ_{cat}	catalyst density, kg/m ³
ρ_{gas}	gas-mixture density, kg/m ³
$\bar{\tau}_p$	mean gas residence time in the reactor, s
$\Phi(x, t)$	switching function for the reaction term based on the thermodynamic condition

Acronyms:

BDF	backward differentiation formulae
CC	coal char
DME	dimethyl ether
DRM	dry reforming of methane

GM	grain model
LHV	lower heating value
MOL	method of lines
NDF	numerical differentiation formulae
ODE	ordinary differential equation
RPM	random pore model
RWGS	reverse water-gas shift
VM	volumetric model

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