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Mathematical modelling of fixed bed catalytic reactors in the dry methane reforming process

Michał Lewak*

Warsaw University of Technology, Faculty of Chemical and Process Engineering, Waryńskiego 1, 00-645 Warszawa, Poland

*** Corresponding author, e-mail:**
michal.lewak@pw.edu.pl

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Abstract

Dry reforming of methane is one of the stages of dimethyl ether production, which is an interesting alternative to diesel fuel. The main problem in dry reforming of methane is the deposition of carbon on the catalyst. This process blocks the catalyst and thus leads to the need for its regeneration or replacement. Therefore, mathematical modelling to determine the conditions of reforming is a key issue that helps to determine the appropriate conditions for the process. In this work, two issues were focused on. The first issue concerned determining the conditions of the reactor wall temperature T_{wall} and the total pressure P_{total} at which the reaction is carried out on the degrees of methane and carbon dioxide conversion. The second issue concerned the influence of T_{wall} and P_{total} on the total mass of carbon deposited on the catalyst. Another goal of this article was to determine the reactor operating conditions in which the deposition of carbon is significantly lower.

Keywords

dry methane reforming, fixed bed reactor, reactions over NiO/Al_2O_3 catalyst, carbon deposition on the catalyst

1. INTRODUCTION

The search for a replacement fuel for diesel is a key issue in today's world. Therefore, an interesting replacement for diesel fuel may be DME. Dimethyl ether is produced from synthesis gas and is a very promising fuel that can power diesel engines. DME has a cetane number between 55–60, and diesel fuel 52 (Putrasari and Lim, 2022), which makes it a better fuel in diesel engines. A higher cetane number means more stable fuel combustion in the engine and greater control over the ignition process of the mixture. Additionally, DME does not contain a solid, which would have to be additionally purified. Since diesel fuel contains solid particles, it must be purified. Another advantage of DME is the lack of sulphur content, which is responsible for the increased generation of soot particles. The lack of sulphur has a positive effect on the service life of the particulate filter. As shown by the latest studies comparing DME and diesel fuel, the former has much better flammability properties in diesel engines (Sonawane and Agarwal, 2023). The advantage of this fuel is that it is easier to feed it to the combustion chamber because, after evaporation, DME does not require a complicated injection system like diesel fuel does. However, DME has three main disadvantages; the first is a lower value of the so-called lower heating value $LHV = 28.80$ MJ/kg compared to diesel fuel $LHV = 42.70$ MJ/kg. This will result in higher DME consumption compared to diesel fuel when travelling the same distance. The second disadvantage is a much lower value of the kinematic viscosity coefficient, which affects the service life of pistons and cylinders in the diesel engine and injectors (Putrasari and Lim, 2022). The last disadvantage is the insufficient availability of this fuel on the market, which is why car manufacturers do not introduce the required modifications in diesel engines so that DME can be used instead of diesel fuel.

The main problem with the availability of this fuel on the market is the problem of profitable production on a global scale. There are two main methods of obtaining DME. The first method involves a catalytic reaction in which hydrogen and carbon monoxide are converted into methanol. The process is carried out in the temperature range from 453.15 K to 613.15 K and in the pressure range from 15 bar to 90 bar. The reactions are mainly catalysed on $Cu/ZnO/Al_2O_3$ catalysts (Portha et al., 2017). In the next stage, methanol is dehydrated to DME in the temperature range from 373.15 K to 573.15 K and under pressure from 10 bar to 30 bar. The synthesis of the direct reaction from synthesis gas to dimethyl ether requires a slightly different type of catalyst than the indirect process (Giuliano et al., 2021). In the direct method, the Al_2O_3-based catalysts must be appropriately modified to eliminate the methanol production step. The second type of method is in the research phase and has not yet reached a fully industrial form. The content of metals and the type of metal covering the aluminium oxide is different than in the catalysts used in indirect methods (Sobczak et al., 2022). In both methods, the main substrate used for the production of DME is synthesis gas, i.e. a mixture of carbon monoxide and hydrogen. Synthesis gas on an industrial scale is produced by three methods: SMR (steam reforming of methane), DMR (dry reforming of methane) and POx (partial oxidation of methane). This article deals with the process of DMR in terms of process conditions ensuring appropriately high degrees of methane and carbon dioxide reaction with the lowest possible degree of carbon deposition on the catalyst. For this purpose, numerical simulations of a flow reactor with a fixed catalyst bed will be used. Methane reforming carried out with the use of carbon dioxide DMR takes place mainly on solid catalysts in which the carrier is Al_2O_3 with nickel or nickel oxide superficially applied to it. In the case of nickel oxide, before starting the reforming reaction, the catalyst must be activated in which nickel oxide is reduced to atomic nickel. Methane reforming with carbon dioxide proceeds according to the stoichiometric equation:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2; \quad \Delta H_{r1} = 247 \text{ kJ/mol} \tag{1}$$

Dry Methane Reforming reaction is accompanied by unfavourable chemical reactions. One of them is the so-called Reverse Water Gas Shift (RWGS) reaction, which proceeds according to the stoichiometric equation:

$$CO_2 + H_2 \leftrightarrow CO + H_2O; \quad \Delta H_{r2} = 41.7 \text{ kJ/mol} \tag{2}$$

The RWGS reaction consumes carbon dioxide and one of the key products of the DMR reaction, i.e. hydrogen. The RWGS reaction produces an excess of carbon monoxide in relation to hydrogen. This is unfavourable because it changes the composition of the CO/H_2 substrates needed to produce DME. In addition, the RWGS reaction is an endothermic process that requires additional heating of the reactor. This increases operating costs. There are three more unfavourable reactions in which the catalyst is deactivated by carbon deposition on the surface. One of them is the unfavourable reaction of methane decomposition, which proceeds according to the stoichiometric equation:

$$CH_4 \leftrightarrow C_{(s)} + 2H_2; \quad \Delta H_{r3} = 74.9 \text{ kJ/mol} \tag{3}$$

Subsequent adverse reactions proceed according to the equations:

$$C_{(s)} + H_2O \leftrightarrow CO + H_2; \quad \Delta H_{r4} = 131.3 \text{ kJ/mol} \tag{4}$$

$$C_{(s)} + CO_2 \leftrightarrow 2CO; \quad \Delta H_{r5} = 172 \text{ kJ/mol} \tag{5}$$

These reactions ((4) and (5)) occur mainly in the direction of substrates and are written in this form because they are represented in the kinetic models included in the literature (see Equations (6)–(10)). All chemical reactions that accompany the DMR reaction are reversible and strongly endothermic. This makes the process challenging to conduct and affects its operating costs. Due to the reversibility of all chemical reactions and the need to heat the reactor, the entire process requires control during the reforming process. Numerical simulations should precede determining the best reactor operating conditions i.e. P_{total} and T_{wall}. They allow estimation of the process conditions in which it is advantageous to conduct the reaction. Methane reforming reactions are carried out in flow reactors with a filling, which is a non-porous heterogeneous catalyst. The catalysts used for the methane reforming process are non-porous because carbon deposition would cause their easy clogging. Analysis of the data in the literature on the subject shows that only catalysts containing nickel or nickel oxide immobilised on the side surface of Al_2O_3 sinter are used on an industrial scale. In this type of catalyst, internal diffusion is not needed to transport reactants to the catalyst surface.

Mathematical modelling related to syngas production risks underestimating the catalyst deactivation phenomenon in numerical simulations. The main problem in this mathematical model type is carbon deposition on the catalyst. This is the main problem that arises with the mathematical modelling of DMR using CFD techniques. Therefore, the use of CFD methods should be preceded by a numerical analysis of a specific model of the process kinetics. This article carried out an analysis to determine the T_{wall} and P_{total} conditions in which relatively little carbon is formed. Moreover, such ranges of process parameters should be used for further simulations based on CFD methods. The analysis of scientific articles dealing with the simulation of the synthesis gas production process in DMR reactions shows that there are no articles related to the influence of process parameters on the formation of carbon in this process.

2. KINETIC MODEL OF THE DMR REACTION

From the literature review on kinetic models developed to describe the DMR reaction process (see Equations (1)–(5)), an approach based on modelling continuous tubular reactors seems to be used. This is the main type of reactor used in the industrial process because it allows for better control of the carbon deposition process on the catalyst. The increase of pressure in the reactor is a signal related to carbon deposition. Reactors are filled with a catalyst and kinetic models are developed based on the results of gas concentrations at the inlet and outlet of the reactor. These are, therefore, pseudo-homogeneous kinetic models describing the total process of adsorption, reaction and desorption in a reactor with a fixed bed of catalysts.

The total rate of the reaction described by stoichiometric equations (see Equations (1)–(5)) is influenced by mass transport mechanisms such as convection and diffusion from the depth of the gas phase to the catalyst surface. In addition, adsorption of gaseous reactants on the catalyst surface, chemical reaction, desorption of products and their diffusion and convection from the boundary layer to the depth of the gas phase. Nevertheless, our own studies (Cherbański et al., 2021) show that this type of catalyst and the conditions of the process can be successfully described by a kinetic model, including adsorption/desorption and chemical reaction mechanisms. This indicates that the other mass transport mechanisms described do not affect the total reaction rate.

Therefore, simplified kinetic models are sought that correctly describe the course of the reaction without going into the description of the mass transport mechanisms. This is one of the reasons why the literature contains almost exclusively kinetic models based on the pseudo-homogeneous kinetic model of a tubular reactor with a fixed bed. In these kinetic models, the main role is played by the catalyst used in the reaction. In this case, Al_2O_3 is mainly used as a carrier, on which an appropriate amount of the metal catalysing the process is applied. The content of additives improves the thermal resistance of the catalyst and reduces carbon deposition. Kinetic models of the methane reforming reaction are, therefore, dependent on the type and content of the metal that catalyses the reactions. In industrial applications, due to the costs, mainly catalysts containing nickel or nickel oxide are used. The use of nickel oxide requires the activation procedure of the catalyst. The use of a given kinetic model for an inadequately reduced catalyst can lead to significant errors between the simulation and the course of the actual process carried out on an inadequately prepared catalyst. Kinetic models for Ni/SiO_2, TiO_2, MgO catalysts or activated carbon are presented in the work (Bradford and Vannice, 1996). The kinetic model of the DMR reaction carried out on the Ni/Al_2O_3 catalyst is proposed in the publication (Benguerba et al., 2015). The concept of using Pt+Ni/PrSmCeZrO/YSZ catalysts seems quite interesting, although their use in industry is not yet possible mainly due to their high production costs (Bobrova et al., 2016). The analysis of publications in the Web of Science database after searching for publications with the words "kinetic dry reforming" in the title shows that experimental studies related to the search for kinetic models describing DMR are still relevant (shown in Fig. 1). The interest of scientists in studying the kinetics of DMR reactions is related to the search for new, better catalysts that allow for the synthesis of gas production reactions under given process conditions and, at the same time, reduce the share of reactions related to carbon deposition on the catalyst.

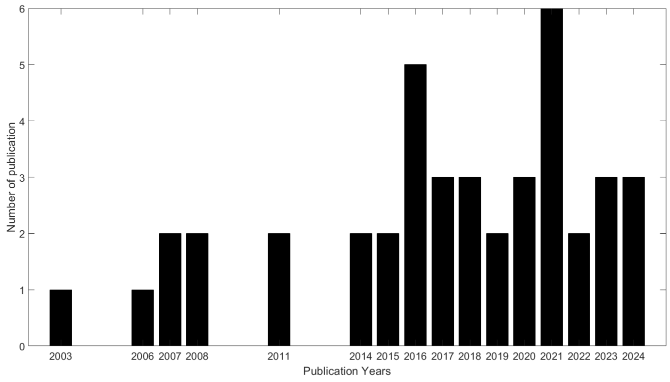

Figure 1. Number of scientific publications related to the study of DMR kinetics according to Web of Science.

Below, a kinetic model of the dry reforming process of methane with unfavourable reactions is presented. This mathematical model is applicable wherever the internal diffusion resistance process in the catalyst pores does not affect the total rate of the process. The kinetic model developed in (Benguerba et al., 2015) was used for the numerical simulations presented in this paper. The total rate of the synthesis gas production reaction (see also Eq. (1)) and the RWGS reaction can be written as follows:

$$r_1 = \frac{k_1 K_{CO2,1} K_{CH4,1} p_{CH4} p_{CO2}}{\left(1 + K_{CO2,1} p_{CO2} + K_{CH4,1} p_{CH4}\right)^2} \left(1 - \frac{\left(p_{CO} p_{H2}\right)^2}{K_{p1} p_{CH4} p_{CO2}}\right) \tag{6}$$

$$r_2 = \frac{k_2 K_{CO2,2} K_{H2,2} p_{CO2} p_{H2}}{\left(1 + K_{CO2,2} p_{CO2} + K_{H2,2} p_{H2}\right)^2} \left(1 - \frac{p_{CO} p_{H2O}}{K_{p2} p_{CO2} p_{H2}}\right) \tag{7}$$

The total reaction rate describing the formation or disappearance of carbon (see Equations (3)–(5)) is expressed by the relations:

$$r_3 = \frac{k_3}{\left(1 + K_{CH4,3} p_{CH4} + \frac{p_{H2}^{1.5}}{K_{H2,3}}\right)^2} \left(p_{CH4} - \frac{p_{H2}^2}{K_{p3}}\right) \tag{8}$$

$$r_4 = \frac{\frac{k_4}{K_{H2O,4}}}{\left(1 + K_{CH4,4} p_{CH4} + \frac{p_{H2O}}{K_{H2O,4} p_{H2}} + \frac{p_{H2}^{1.5}}{K_{H2,4}}\right)^2} \left(\frac{p_{H2O}}{p_{H2}} - \frac{p_{CO}}{K_{p4}}\right) \tag{9}$$

$$r_5 = \frac{\frac{k_5}{K_{CO,5} K_{CO2,5}}}{\left(1 + K_{CO,5} p_{CO} + \frac{p_{CO2}}{K_{CO,5} K_{CO2,5} p_{CO}}\right)^2} \left(\frac{p_{CO2}}{p_{CO}} - \frac{p_{CO}}{K_{p5}}\right) \tag{10}$$

This method of mathematical description of reactions accompanying the process of dry methane reforming is not an isolated one in the literature. Coal deposition reactions are described using partial pressures of gases without the participation of coal itself. This carries the risk of the reaction described by Equations (3), (4) or (5) towards coal consumption without its presence in the reactor. This means that kinetic models must be experimentally validated before being used for a specific problem. Therefore, a number of experiments were carried out in which the DMR reaction process was studied in the experimental reactor. The adsorption constants and equilibrium constants used in the kinetic model were taken from the work (Benguerba et al., 2015). Experiments were carried out in a fixed-bed tubular reactor to determine the kinetic constants (k_1, k_2, k_3, k_4, k_5) of the reaction rate associated with the dry methane reforming process. As part of these experiments, profiles of reactant concentrations at the reactor outlet were obtained depending on the total pressure in the system and the temperature in the furnace. The results obtained in this way allowed, based on a simple one-dimensional mathematical model, to determine the values of the kinetic constants (see constants k_1, k_2, k_3, k_4) describing the course of the DMR reaction. In the opinion of the author of this article, the good agreement of the kinetic model with the experimental data justifies the use of this simple model in the simulation of reactor operation for the production of synthesis gas. During the tests, there were no significant changes in hydrogen and carbon monoxide composition at the reactor outlet. No significant increases in the reactor's total pressure were observed, indicating that the phenomenon of carbon deposition on the catalyst was insignificant. Details about the experiments can be found in the work (Cherbański et al., 2021).

3. ONE-DIMENSIONAL MATHEMATICAL MODEL OF A FIXED BED REACTOR

The essential requirement for mathematical models is to calculate actual experimental results. In chemical reactor engineering, the mathematical model supports the designer in developing guidelines for constructing an actual device to operate efficiently. It is not without reason that numerical simulations describing the operation of chemical reactors have become one of the main tools designers and scientists use in constructing such devices. Two reactors were built to conduct the dry methane reforming process as part of this work. The results presented in this work contributed to defining guidelines for the constructed large-scale laboratory reactor and a semi-technical scale reactor. A mathematical model is good when two conditions are met. The first condition concerns the model describing the kinetics of the reaction; if the kinetic model correctly describes the process's course, the reactor's mathematical model will interact well with the real process. Fulfilling the second condition is a form of compromise between the mechanisms of mass, momentum and energy transport taken into account and the time needed to obtain results related to the numerically calculated system of differential equations. The analysis of the mass and energy-momentum transport mechanisms related to the case of a reactor in which the DMR process is carried out allows for the introduction of simplifications. The first simplification concerns the omission of the mechanism related to diffusion mass transport. The residence time of the gas in the reactor is short (of the order of a few seconds), so the diffusion process will not contribute much to this issue, and its inclusion will cause problems with the convergence of calculations. Including a phenomenon that generates a minimal mass flux in the mathematical model will affect the numerical discrepancy. A similar thing happens with the mass dispersion process in this reactor: the size of the catalyst and its quantity (a few catalyst lumps) prevent this phenomenon from affecting the transport of components. Including it in the model is pointless and will lead to a numerical discrepancy. The catalyst is non-porous, which leads to the conclusion that the reactions occur on its surface, so internal diffusion does not affect the course of the process. The same applies to heat transport mechanisms; the literature correlation used in the simulations presented in this article allows us to determine the total heat transfer coefficient from the reactor wall to the bed. The high thermal conductivity coefficients of the catalyst material (1273 K, which is 6.16 W/(mK)) allow us to ignore the temperature drop on the catalyst wall. This leads to the conclusion that a one-dimensional model is sufficient to describe this reactor's energy and mass transport. A limitation of the mathematical model proposed in this work is the failure to consider the phenomenon of energy transport by electromagnetic radiation. A one-dimensional model cannot describe thermal radiation. Therefore, the proposed model does not estimate a certain amount of energy resulting from radiation. What effect does this have on the process? First, the catalyst shape temperature will be slightly higher in reality than in the model presented here. This leads to the conclusion that the phenomena related to carbon deposition in this model will be more intense than in reality because the temperature at the catalyst surface will be higher. Therefore, less carbon will be deposited on it. There is another reason for using such a simple mathematical model. It is related to the use of CFD techniques. In such methods, we are not able to describe the process of carbon deposition on the catalyst, and this phenomenon has a key impact on the operating costs of the reactor. Therefore, it was decided to check the best ranges of reactor operation (i.e. T_{wall} and P_{total}) in which the least carbon is produced, and these ranges will be used to determine the effect of process conditions on the course of the process using CFD simulations. The results of this procedure will be presented in a separate publication.

Selecting an appropriate mathematical model to describe the methane reforming process is not simple. It will always be associated with a compromise between the time needed to perform the calculations and the degree of complexity of the mathematical model. The problem of mathematical modelling of such issues using CFD techniques was described in detail in the article (Kaydouh et al., 2024). However, CFD models are based exclusively on kinetic models developed using experimental studies supported by simple one-dimensional models (Benguerba et al., 2015; Olsbye et al., 1997). The selection of an appropriate kinetic model is dictated by the catalyst's shape and degree of fragmentation. A similar approach to the problem description can be found in the work (Maqbool et al., 2021), where the authors focused on a one-dimensional description of the process without giving up the mechanisms of convection and diffusion. A similar modification of the multidimensional model to the one-dimensional model was used to describe the steam-reforming process of methane (Fabrik et al., 2023). The mathematical model proposed in this paper is quite often used to simulate the operation of a reactor producing synthesis gas (Yang and Twaiq, 2017). The mathematical description proposed in this work was verified in experimental studies (Cherbański et al., 2021). It was, therefore, used to determine the effect of T_{wall} and P_{total} on the total amount of carbon deposited on the catalyst. Therefore, the one-dimensional mathematical model of the tubular reactor presented in (Froment, 1967) was used in the numerical simulations. The use of a one-dimensional model entails the need to meet the following simplifying assumptions:

- The catalyst is non-porous, therefore internal diffusion has no effect on mass transport in the process.
- The reaction takes place on the outer surface of the catalyst.
- There is no resistance to mass transfer to and from the catalyst surface.
- There are no pressure drops in the reactor.
- The thermal conductivity coefficient of Al_2O_3 at 573 K is 17.24 W/(mK), and at 1273 K, it is 6.16 W/(mK). Therefore, it can be assumed that the catalyst temperature has the same value as the gas temperature (Touloukian, 1967).
- There is no heat conduction resistance through the tubular reactor wall.
- The temperature on the surface of the inner wall is constant and equal to the temperature of the outer wall.
- The description of the DMR reaction process can be described by Equations (6)–(10).
- There is no axial and radial dispersion in the reactor.
- Radiative heat transport is not taken into account.

The validity of using such a simple mathematical model for a catalytic reactor filled with spheres was confirmed in studies related to the development of a kinetic model of the dry methane reforming reaction (Cherbański et al., 2021). The kinetic model used in this work was implemented for the problem of a similar reactor but filled with a spherical catalyst (see Fig. 2).

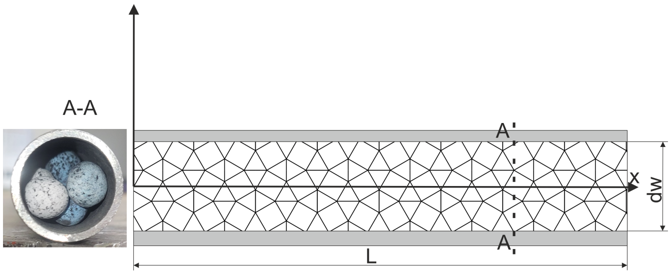

Figure 2. Fixed bed reactor schematic.

Its properties were identical to the catalyst with the help of which the kinetics of the dry methane reforming reaction was developed. The disadvantage of the kinetic model implemented in this work is the fact that it does not take into account the effect of carbon deposition on the catalyst efficiency. There are no advanced mathematical models in the literature that satisfactorily describe the catalyst deactivation process during methane reforming. Therefore, the focus was on using the kinetic model to analyse the effect of process conditions on the course of the process. The one-dimensional kinetic model results from the balance of molar fluxes of Ni reactants and the energy balance represented by the enthalpy of the gas mixture h.

$$\varepsilon \frac{\mathrm{d}N_i}{\mathrm{d}x} = \sum_{j=1}^{N} \nu_{ij} R_j \rho_{\mathrm{cat}} (1-\varepsilon) F \tag{11}$$

$$\varepsilon \frac{\mathrm{d}h}{\mathrm{d}x} = \sum_{j=1}^{N} (-\Delta H_j) R_j \rho_{\mathrm{cat}} (1-\varepsilon) F + U_w \pi d_w (T - T_w) \tag{12}$$

In the process, the total number of moles of reactants changes, therefore the molar balance is based on the molar flows of reactants and the energy balance on the enthalpy of the gas mixture:

$$N_i = F u C_i \tag{13}$$

$$y_i = \frac{N_i}{\sum\limits_{j=1}^{M} N_j} \tag{14}$$

The total pressure in the reactor is constant and equal to P_{total} and the changes in the partial pressures of the reactants can be expressed by the relations:

$$p_i = y_i P_{\mathrm{total}} \tag{15}$$

The values of the reaction enthalpy were calculated according to Hess's law using the approximation of the enthalpy of the individual compounds as a function of temperature. In turn, the following relationship was used to calculate the specific heat of the mixture C_p:

$$C_{p\,\mathrm{mix}} = \sum_{i=1}^{M} y_i C_{p\,i}(T) \tag{16}$$

The $C_{p\,i}$ values for pure components were taken from the NIST database (NIST, 2024). The enthalpy values of the reactants as a function of temperature were used from the NIST database (NIST, 2024). The enthalpy of the gas mixture allows us to find the gas temperature in the form of the relationship:

$$T = \frac{h}{u \varrho_{\mathrm{gas}} F C p_{\mathrm{mix}}(T_{\mathrm{wall}})} + T_{\mathrm{amb}} \tag{17}$$

In order to determine the temperature changes based on the gas enthalpy, a certain simplification was used. It was assumed that the specific heat of pure reactants would be calculated at the wall temperature T_{wall}. Such a simplification allowed direct calculation of the temperature at each integration step, without the need for tedious numerical calculations of the nonlinear equation in order to find the gas temperature at each integration step of partial differential equations. The gas density at each integration step was determined using the Redlich-Kwong equation and the gaseous reactant mixing rules. The Herning and Zipperer formulas were used to determine the viscosity of the gas mixture. The heat conduction coefficient of the gas mixture was calculated additively with the correction proposed by Brokaw. The correlation of Martin and Nilles (1993) was chosen to describe the heat exchange process between the reactor wall and the fluid and catalyst particles (Derkx, 1995):

$1000 > Pe_d = (ud_p)/\lambda_f > 10$

$$\mathrm{Nu}_{w0} = \left(1.3 + 5\frac{dp}{Dw}\right)\frac{\lambda_{\mathrm{cat}}}{\lambda_f} \tag{18}$$

$$\mathrm{Nu} = \mathrm{Nu}_{w0} + 0.19\mathrm{Re}^{0.75}\mathrm{Pr}^{0.33} \tag{19}$$

Mathematical modelling of the heat transfer phenomenon in a catalytic reactor can be based on direct CFD simulations of the real catalyst shapes or using correlations developed experimentally. The use of literature correlations allows the use of a one-dimensional mathematical model to describe the energy transport process in reactors with a catalytic bed. This allows mathematical modelling using faster computational tools than CFD methods. The correlations described by Equations (17)–(18) were used in the simulations presented in this paper. This correlation can be applied to spherical, cylindrical and hollow cylinder fillings. The catalyst consists of spherical Al_2O_3 lumps on which about 20% nickel was deposited, mainly on the side surface of the catalyst because Al_2O_3 is characterized by a very small internal pore volume of about 2 m^2/g. To describe the changes in specific conductivity with temperature, the approximation of experimental data included in the paper (Touloukian, 1967) was used.

4. SIMULATION RESULTS

The paper investigates the influence of pressure and wall temperature on the course of the dry reforming process of methane. The kinetic model of the chemical reaction presented in this paper was used for this purpose. The kinetic model is simple enough to be implemented in numerical simulations, which allows to obtain fast results of concentration and temperature distributions in the reactor. Table 1 presents the individual dimensions of the reactor and the diameter of the spherical catalyst particles.

Table 1. Fixed bed reactor process parameters.

D_z [mm]	D_w [mm]	L [mm]	d_p [mm]
25.4	21.6	630	9

In the numerical simulations, it was assumed that the reactor wall temperature is constant and equal to T_{wall}. This assumption is correct for reactors made of materials that conduct heat well, in which the wall thickness is so small that the thermal resistance of conduction is negligible. In such a case it can be assumed that the temperature in the reactor wall has a constant value. Table 2 presents the values of the temperatures T_{wall} and the total pressure P_{total} that were used in the numerical simulations.

Table 2. The parameters of the numerical simulation process for a given pressure P_{total} where the wall temperature was variable in increments of $\Delta T_{\mathrm{wall}} = 10$ K.

Name	T_{wall} range [K]	P_{total} [bar]
P1	573; 583; . . . ; 1273	1
P2	573; 583; . . . ; 1273	2
P3	573; 583; . . . ; 1273	3
P4	573; 583; . . . ; 1273	4
P5	573; 583; . . . ; 1273	5

The wall temperature was selected as follows. For a fixed total pressure in the reactor and a constant molar flow of methane and carbon dioxide at the reactor inlet, the wall temperature T_{wall} was changed in the range from 573 K to 1273 K with a temperature step of 10K (see Table 2). The ode23s method, which is implemented in Matlab 2024a, was used to perform the simulation. The ode23s method contains instructions for numerical integration of systems of ordinary differential equations using Rosenbrock algorithms. This is a so-called closed numerical method and is used for rigid systems of differential equations. The following parameters were used for numerical calculations: relative error $RelTol = 10^{-4}$, absolute error $AbsTol = 10^{-5}$, maximum integration step $MaxStep = 5 \cdot 10^{-3}$ m. The figure below shows the mole fraction distribution of gaseous reactants along the reactor for the case when the wall temperature is equal to $T_{\mathrm{wall}} = 1273$ K. At temperatures above 1000 K, the reaction equilibrium is shifted towards the products, which results in almost complete conversion of gaseous reactants. The concentration of hydrogen at the reactor outlet is slightly lower than the concentration of carbon monoxide, because hydrogen is consumed in the RWGS reaction. This is an unfavourable situation, because one of the important components of the synthesis gas, which is hydrogen, is consumed and water vapour and carbon monoxide are produced. This makes the production costs of fuel such as DME higher. From the analysis of the numerical simulations performed, it is clear that the increase in the temperature of the reactants shifts the equilibrium of the RWGS reaction towards the reactants, which results in the conversion of water vapour in the process. And this is not due to the reaction between water vapour and coal (see Equation (4)), because this reaction takes place towards the production of coal and is unfavourable. This obviously increases the costs of syngas production by reducing the amount of gas produced from the same amounts of substrates. Additionally, the costs are increased by the need to regenerate the catalyst by removing the carbon accumulated on its surface. This process must be performed frequently enough and at the right time so that the accumulated carbon does not completely destroy the heterogeneous catalyst and does not stop the reforming reaction. The appropriate reactor operation time is a key parameter that affects the profitability of the entire process. Therefore, determining the total amount of carbon produced in the process is an important process parameter.

The key parameter of the reactor operation is the average residence time $\overline{\tau}_p$ of the reactants calculated as the arithmetic mean of the instantaneous residence times along the catalytic reactor. This is because the molar flow of gases changes during the chemical reaction, which results in a change of the speed at which the gas travels through the catalytic reactor. To sum up, the increase in water concentration in the first few centimetres from the reactor inlet results from the course of the RWGS reaction and the reaction producing coal (see Equation (4)). Only an increase in the gas temperature causes the reaction to shift towards the substrates. The numerical analysis of the equations shows that the carbon deposition reactions occur mainly in the direction of its production. It should be added that this is the maximum operating temperature of this catalyst 1273 K. The next figure presents the gas temperature distribution along the reactor (see Fig. 4). The value of the gas enthalpy resulting from the inlet composition at the wall temperature was selected as the inlet condition. A sudden drop in gas temperature close to the reactor inlet is associated with a very rapid increase in the reaction rate, as evidenced by the vertical lines of changes in the mole fractions of reactants at the reactor inlet (see Fig. 3). Strongly endothermic reactions remove heat from the system, which causes the gas and catalyst temperatures to drop where the reactions are taking place. Therefore, a few centimetres from the reactor inlet, the greatest drop in gas and catalyst temperature occurs. It is important that the reactor wall temperature T_{wall} is high enough so that heat absorption by the reactions does not cause a significant drop in gas temperature.

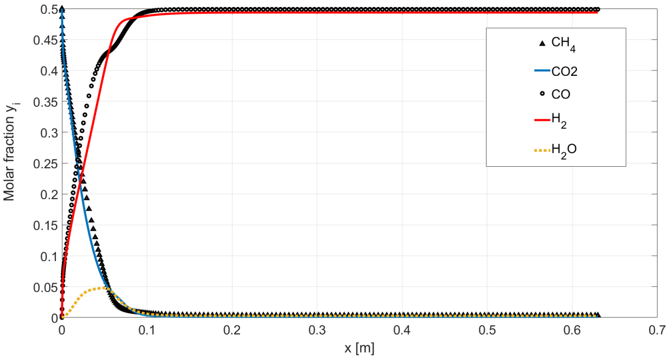

Figure 3. Molar fraction distribution along the reactor, $T_{\text{wall}} = 1273$ K, $N_{\text{CH4 in}} = N_{\text{CO2 in}} = 0.5$ mol/min, $\overline{\tau}_p = 0.743$ s.

A significant reduction in gas temperature will slow down the reaction to such an extent that chemical equilibrium will not be achieved before the gas leaves the reactor. As a result, the reactor will not be fully utilized for the production of synthesis gas. One of the significant problems that arise during mathematical modelling of reactions related to DMR is the deposition of carbon on the catalyst. The course of chemical reactions and the equilibrium achieved in the process depend on the temperature and total pressure. This makes the catalyst lifetime strongly dependent on the temperature and pressure at which the reactions are conducted. The main problem with the mathematical description of the process is determining the changes in the amount of carbon formed during chemical reactions. Therefore, the construction of the kinetic model is done using experimental data measured at the reactor outlet. On this basis, the experimental data are adjusted to the kinetic model using nonlinear regression methods. Apart from the obvious advantages, this approach also has disadvantages. The main disadvantage is the lack of control in the kinetic model of the actual number of moles of carbon formed in the process. This can cause distortions of the kinetic model. To prevent this, the kinetic model must not be used outside the pressure and temperature range for which it was developed. And if such a model is extrapolated, it must be realized that the results obtained in the kinetic model may differ from the actual results of the reaction. The key parameter, apart from the conversion rates, is the total amount of carbon produced in the process and the average residence time $\overline{\tau}_p$. It gives a qualitative idea of the reactor's ability to produce synthesis gas and the need to regenerate the catalyst after a multiple of the residence time of the reactants in the reactor. The multiple of the residence time T depends on the carbon production rate and the surface area of the catalyst used in the process. The total mass balance in the reactor was used to determine the instantaneous value of carbon produced in the process. Figure 5 presents three curves illustrating the total mass balance in a fixed-bed reactor. The continuous line indicates the total mass flow of reactants that enters the reactor at the inlet and this is a constant value. The dashed line shows the total mass balance calculated in the reactor for the first two reactions, i.e. DMR and RWGS, which illustrates to some extent the error of the numerical method used (no carbon deposition reaction). The circle markers indicate the total instantaneous mass balance resulting from the course of five reversible reactions (reactions described by Equations (1)–(5)). The simulations confirmed that the mass loss results from the course of the reaction towards coal production (reactions described by Equations (3)–(5)) and not from numerical errors. This has been unequivocally verified.

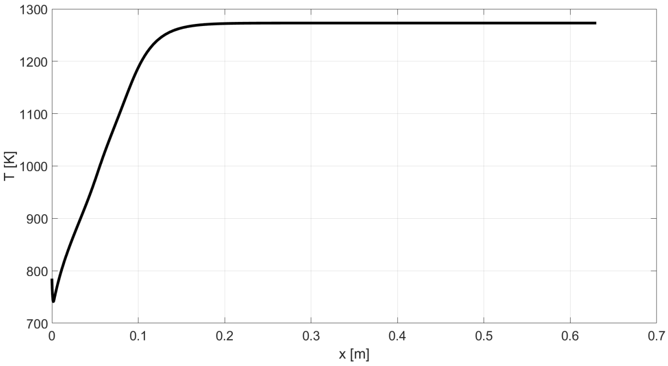

Figure 4. Temperature distribution along the reactor, $T_{\text{wall}} = 1273$ K, $N_{\text{CH4 in}} = N_{\text{CO2 in}} = 0.5$ mol/min, $\overline{\tau}_p = 0.743$ s.

Therefore, the momentary mass loss is related to the deposition of carbon on the catalyst, which allows to determine the momentary amounts of carbon mass in the reactor. And thus allows to determine the total amount of carbon mass

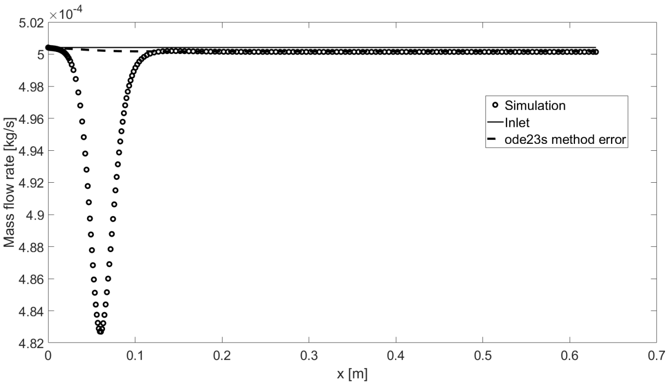

Figure 5. Total mass balance in reactor, $T_{\text{wall}} = 1273$ K, $N_{\text{CH4 in}} = N_{\text{CO2 in}} = 0.5$ mol/min, $\overline{\tau}_p = 0.743$ s.

that will be created in the process during the residence time τ_p. The mass of carbon that is created and the total mass of carbon deposited on the catalyst have a direct impact on the course of the process. Figure 6 presents how the carbon deposition on the catalyst changes along the reactor. As can be seen from the graphs below, the amount of mass that is deposited on the catalyst is the greatest at a distance of a few centimetres from the inlet. This leads to the conclusion that the reactor got clogged in close proximity to the inlet. Catalyst clogging may result in a sudden and unexpected increase in pressure *a* in the reactor. This is a very dangerous phenomenon and should be taken into account when determining the reactor operating time. In order to prevent possible leaks in the reactor, which may lead to fires or explosions.

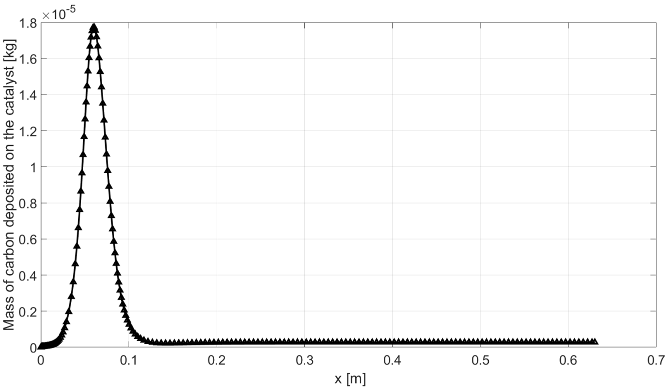

Figure 6. Mass distribution of carbon deposited on the catalyst, $T_{\text{wall}} = 1273$ K, $N_{\text{CH4 in}} = N_{\text{CO2 in}} = 0.5$ mol/min, $\overline{\tau_p} = 0.743$ s.

To analyse the results of numerical simulations, two parameters characterizing the process were determined: the degree of methane conversion α_{CH4}, the degree of carbon dioxide conversion α_{CO2}:

$$\alpha_{\text{CH4}} = \frac{N_{\text{CH4 in}} - N_{\text{CH4}}(x)}{N_{\text{CH4 in}}} \tag{20}$$

$$\alpha_{\text{CO2}} = \frac{N_{\text{CO2 in}} - N_{\text{CO2}}(x)}{N_{\text{CO2 in}}} \tag{21}$$

Another key process parameter used to analyse the results is the instantaneous and average residence time in the reactor:

$$\tau_p(x) = \frac{L - x}{\text{velocity}(x)} \tag{22}$$

$$\overline{\tau}_p = \frac{\sum\limits_{i=1}^{N} \tau_{p\,i}}{N} \tag{23}$$

Table 2 presents the results of the degree of methane and carbon dioxide conversion at the reactor outlet. Additionally, the ratio of carbon monoxide moles to hydrogen at the reactor outlet is included. These parameters allow us to assess the efficiency of the reactor for the production of synthesis gas. They are the main parameters characterizing the synthesis gas production process and thus affect the profitability of the DME production process. As can be seen, the increase in the cutting temperature causes an increase in the degree of conversion of both substrates. This is a very positive effect, because it allows for an increase in the reactor efficiency. Interestingly, the increase in temperature affects the reduction of the ratio of desired reaction products at the reactor outlet. This is of key importance for further processes related to the use of both components of synthesis gas for the production of DME. The last two columns contain the average residence times and the total mass of carbon deposited in the reactor during the average residence time (see column 5 of Table 2).

The analysis of the carbon content formed in the reaction as a function of the wall temperature T_{wall} shows that we are dealing with an extreme carbon concentration in the reactor. The higher the wall temperature, the more carbon is produced until a maximum is reached, after which a further increase in the wall temperature T_{wall} causes a decrease in the total mass of carbon produced in the reaction. This is a very positive conclusion from the numerical simulations performed. In the case shown in Table 2, the maximum of deposited carbon is at a wall temperature of about 923 K. At this wall temperature, most carbon will be formed, requiring more frequent reactor downtimes to regenerate the catalyst. Therefore, conducting the reaction at a pressure of $P_{\text{total}} = 101325$ Pa is best carried out near the maximum catalyst operating temperature, i.e. about 1273 K. Then we have the smallest amount of carbon deposition on the catalyst and high degrees of CH_4 and CO_2 reaction. Thanks to this, the process will be more profitable from the economic point of view. The influence of the total pressure P_{total} on the course of the process is illustrated in the further part of the paper. Figure 6 shows the degree of methane conversion at the reactor outlet depending on the wall temperature T_{wall} and the total pressure P_{total}. As can be seen from this figure, the increase in pressure lowers the degree of methane conversion, which is in line with expectations. In the methane reforming reaction (1) and the methane decomposition reaction on the catalyst (3), the increase in pressure shifts the equilibrium of both reactions towards the substrates. Therefore, the increase in pressure at which the

Table 3. The influence of wall temperature on the course of the dry methane reforming reaction $P_{\text{total}} = 101325$ Pa.

T_{wall} [K]	$\alpha_{\text{CH4 out}}$ [–]	$\alpha_{\text{CO2 out}}$ [–]	$y_{\text{CO}/y\text{H2 out}}$ [–]	$\overline{\tau}_p$ [s]	$m_{\text{C total}}$ [kg]
573	0.0044	0.006	1.409	0.1776	0
623	0.0143	0.025	2.235	0.195	$3.00*10^{-6}$
673	0.0372	0.0659	2.346	0.213	$1.50*10^{-5}$
723	0.0808	0.1295	1.934	0.2402	$4.90*\ 10^{-5}$
773	0.1609	0.2262	1.573	0.2704	0.000153
823	0.3115	0.3492	1.16	0.3089	0.000577
873	0.6025	0.4664	0.704	0.3592	0.002179
923	0.8035	0.5712	0.638	0.4283	0.004171
973	0.869	0.7121	0.793	0.4796	0.003804
1023	0.9144	0.8383	0.91	0.528	0.002656
1073	0.9433	0.92	0.974	0.569	0.001679
1123	0.961	0.9628	1.002	0.6158	0.001082
1173	0.9723	0.9826	1.011	0.6658	0.000777
1223	0.9801	0.9916	1.012	0.7137	0.000599
1273	0.9856	0.9957	1.01	0.7522	0.000491

process is carried out results in lower methane conversion coefficients. The increase in pressure in the reactor causes the equilibrium of the reaction between methane and carbon dioxide to shift towards the formation of substrates. Therefore, carrying out the reaction at higher pressures than atmospheric is unfavourable in terms of the efficiency of the DMR reaction. The influence of the wall temperature on the process is also quite obvious, because the increase in the temperature on the wall affects the increase in the temperature of the gas mixture. This results in an increase in the reaction rate at the reactor inlet. In the simulations performed, it was assumed that the temperature of the substrates at the inlet is equal to the wall temperature T_{wall}. Therefore, increasing the gas temperature will result in higher methane conversion rates and this is shown in the graph (see Figure 7).

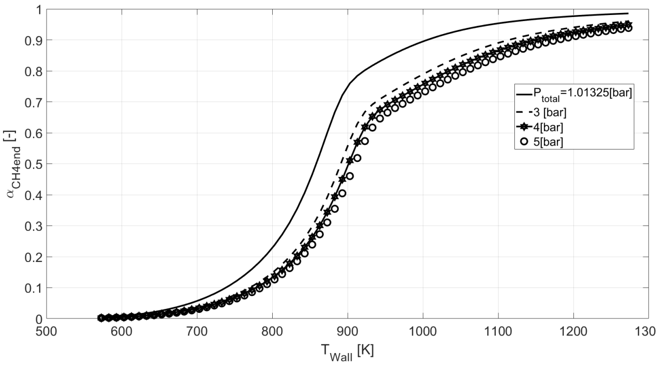

Figure 7. Impact of T_{wall} temperature and total pressure on the CH_4 conversion factor at the reactor outlet, $N_{\text{CH4 in}} = N_{\text{CO2 in}} = 0.5$ mol/min.

The increase or decrease in pressure does not affect the equilibrium course in the RWGS reaction. Therefore, changes in the degree of carbon dioxide conversion as a function of pressure result from the effect of pressure on the equilibrium in the remaining reactions. Analysis of the degree of carbon dioxide conversion shows that the dependence of the pressure effect depends on the products of the DMR reaction, i.e. hydrogen, carbon monoxide and water vapour formed in reaction 4. This can be clearly seen by comparing Figures 7 and 8. Changes in curve 7 are visible in curve 8. Therefore, the highest degrees of CO_2 conversion are obtained for the pressure $P_{\text{total}} = 1.01325$ bar. The increase in the temperature on the reactor wall causes an increase in the carbon dioxide conversion coefficient. And this is caused by the effect of pressure on the course of the DMR reaction and the thermal decomposition reaction of methane. The increase in the reactor wall temperature T_{wall} causes an increase in the degree of carbon dioxide conversion, which results to a certain extent in an increased amount of syngas produced. The profitability of conducting the reaction at high temperatures depends on the amount of carbon formed in this process, which is deposited on the catalyst.

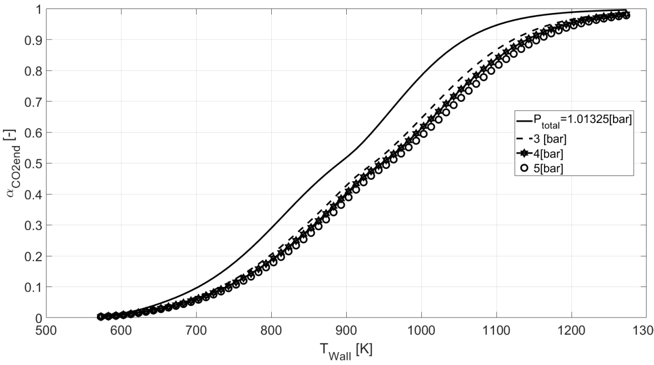

Figure 8. Impact of T_{wall} temperature and total pressure on the CO_2 conversion factor at the reactor outlet, $N_{\text{CH4 in}} = N_{\text{CO2 in}} = 0.5$ mol/min.

Interesting conclusions can be drawn by analysing the effect of the total pressure at which the process is conducted on the total amount of carbon deposited on the catalyst and the effect of the wall temperature T_{wall} (see Fig. 9). For a given pressure, the increase in wall temperature on the total mass of carbon deposited on the catalyst shows a local optimum and this is the maximum of the carbon content that is deposited on the catalyst. This leads to the conclusion that it is more efficient to conduct the process at higher temperatures only after exceeding the temperature at which the total mass of deposited carbon is maximum. Conducting the reaction at lower temperatures allows to reduce the amount of carbon formed but at the cost of low degrees of methane and carbon dioxide reaction (see Fig. 8). This leads to the conclusion that knowledge of the wall temperature at which we deal with the maximum mass of carbon formed is crucial for this process. This is an important conclusion resulting from the numerical simulations performed. In addition, the effect of P_{total} and T_{wall} at which the mass of deposited carbon is maximum is particularly important in the range of $\langle 1 - 2 \rangle$ bar. The increase in pressure causes an increase in the total mass of deposited carbon at a slightly higher temperature T_{wall}. This leads to the conclusion that the increase in total pressure increases production costs at identical degrees of methane and carbon dioxide conversion and additionally the total amount of carbon deposited on the catalyst increases. This leads to more frequent downtimes of the installation in order to regenerate the catalyst. The simulations performed clearly show that below 2 bar less carbon is produced in the process. This is a very important conclusion from the point of view of the profitability of the entire synthesis gas production process.

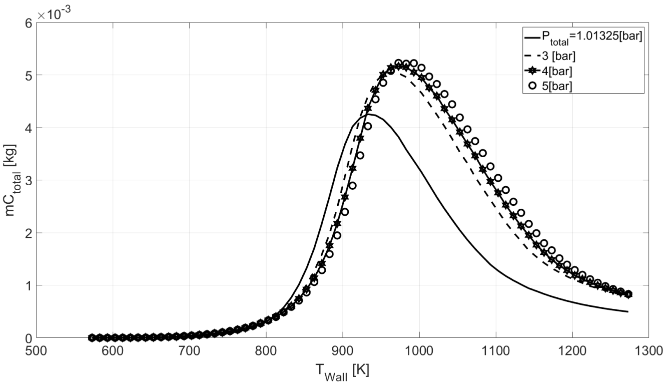

Figure 9. Effect of T_{wall} temperature and total pressure on total mass of carbon deposited on the catalyst, $N_{\mathrm{CH4\,in}} = N_{\mathrm{CO2\,in}} = 0.5$ mol/min.

5. CONCLUSIONS

The vast majority of mathematical models used to describe reactions related to the production of syngas have been developed experimentally based on measurements of gaseous reactant concentrations between the reactor inlet and outlet. A kinetic model of the reaction and adsorption process was proposed on this basis. The kinetic constants for this model were selected using nonlinear regression methods, and the larger the number of constants, the better the fit of the data to the kinetic model. Unfortunately, most of these models assume that the carbon deposition process does not significantly affect the course of the reaction. Therefore, using these kinetic models to simulate the operation of reactors must be supported by an analysis of the amount of carbon produced in the process. Thanks to this, we can estimate the operating time of such a reactor based on the total amount of carbon produced and the residence time. This will allow the implementation of catalyst regeneration procedures. In addition, estimating when such a catalyst should be replaced will be possible so that the reactor does not become clogged during the process due to too much carbon deposited on the catalyst. Therefore, the results of numerical simulations using this type of mathematical model should be approached with caution because deposition determines the operating time of a reactor, and the kinetic model does not directly consider catalyst deactivation. Two valuable conclusions result from the analysis of the simulations performed.

First, conducting the methane reforming reaction at pressures higher than 2 bar is uneconomical and leads to a decrease in the degree of methane and carbon dioxide conversion. At a temperature $T_{\mathrm{wall}} = 1100$ K, the degree of methane conversion is 0.95 and carbon dioxide 0.95 at a total pressure in the system equal to $P_{\mathrm{total}} = 1$ bar. The exact process conducted at a pressure of 5 bar and an identical wall temperature generates a degree of methane conversion at the outlet equal to 0.85 and carbon dioxide at 0.82. In addition, an increase in pressure increases the temperature of the wall at which maximum carbon deposition occurs. The wall temperature at which maximum carbon deposition occurs is $T_{\mathrm{wall}} = 933$ K (at $P_{\mathrm{total}} = 1$ bar), and for $P_{\mathrm{total}} = 5$ bar, T_{wall} at which maximum carbon deposition occurs is 983 K. This is an unfavourable effect that increases the costs of running the process.

The second conclusion is that only after exceeding the temperature T_{wall} at which carbon deposition reaches a maximum it is beneficial to run the process, taking into account the temperature of thermal stability of the catalyst. Running the reaction at high temperature increases the costs of the process and, thus, the costs of DME production. However, higher process temperatures result in equivalent amounts of carbon monoxide and hydrogen, which is advantageous in direct DME production methods (see Table 3). This work is part of the issue related to the search for the best reactor operating conditions while not omitting the phenomenon of carbon deposition, which is often neglected in articles on this process, both in dry and steam reforming of methane. The key to using DME in diesel engines on an industrial scale is to solve the problem of deactivating catalysts, the cost of which is a significant element of the profitability of the entire project.

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SYMBOLS

C_i	concentration of i-th component, mol m^{-3}
Cp_i	heat capacity of i-th components, J $kg^{-1}K^{-1}$
Cp_{mix}	heat capacity mixture, J $kg^{-1}K^{-1}$
D_w	reactor inner diameter, m
D_z	reactor outer diameter, m
d_p	catalyst diameter, m
F	area, m^2
h	enthalpy mixture, J s^{-1}
k_i	reaction rate constant, mol $kg^{-1}s^{-1}$
K_i	adsorption constant rate unit depends on mechanism adsorption i-th component (see in Benguerba et al., 2015)
Kp_j	equilibrium constant rate j-th reaction unit depends on reaction (see in Benguerba et al., 2015)
L	reactor length, m
N_i	molar flux of the i-th component, mol s^{-1}
Nu	Nusselt number
P_{total}	total pressure, bar
p_i	partial pressure of i-th component, bar
Re	Reynolds number
R_j	j-th reaction rate, mol $kg^{-1}s^{-1}$
T_{wall}	wall temperature, K
T	temperature, K
T_{amb}	ambient temperature, K
U_w	overall heat transfer coefficient, $Wm^{-2}K^{-1}$
u	velocity of gas ,$m \cdot s^{-1}$
x	axial coordinate, m
y_i	molar fraction i-th component

Acronyms

DME	dimethyl ether
DMR	dry methane reforming
LHV	lower heating value
RWGS	reverse water gas shift

Greek symbols

α_{CH4}	methane conversion factor
α_{CO2}	carbon dioxide conversion factor
ΔH_j	heat of reaction, J mol^{-1}
ε	porosity
λ_f	heat conductivity of fluid ,$Wm^{-1}K^{-1}$
λ_{cat}	heat conductivity of catalyst, W $m^{-1}K^{-1}$
ρ_{gas}	density of gas, kg m^{-3}
ρ_{cat}	density of catalyst, kg m^{-3}
τ_p	residence time, s

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