Simplified modelling of a fixed bed reactor for catalytic methane combustion

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Abstract
The work concerned the introduction of simplifications in a one-dimensional mathematical model of a chemical reactor. Fecralloy foam with a pore density of 16 PPC (pores per centimetre) was used as catalyst support. The analysed process was the combustion of methane with a typical concentration found in the ventilation air of hard coal mines. The process was carried out using a palladium catalyst.

Keywords
methane combustion, reactor modelling, mine ventilation

1. INTRODUCTION

The poster presented at the EPIC 2023 conference discusses the results of the mathematical modelling of a chemical reactor with a catalyst bed made of Fecralloy® metal foam with a pore density of 16 PPC (pores per centimetre). Experimental research and mathematical modelling concern a reactor used to remove methane present in the ventilation air of hard coal mines in Poland. Methane is a dangerous greenhouse gas with the potential to create an effect (GWP) over a hundred years of ~ 27. From the ventilation systems of underground mines to the atmosphere huge amounts of this gas are released. Reducing its emissions into the atmosphere not only contributes to the protection of the natural environment, but also improves the economic situation of the mine, because emissions into the atmosphere are subject to fees, and surpluses above the norms are subject to additional financial penalties. Currently for methane disposal mainly thermal methods are used (Pawlaczyk-Kurek and Suwak, 2021), which require conducting the process at temperatures above $800\,°C$. An alternative to thermal methods is the catalytic oxidation of methane (Gancarczyk et al., 2018). A new type of catalytic reactor, characterized by high efficiency, is still sought. One of the promising concepts seems to be the use of solid foams as a catalyst carrier. However, when a new reactor is designed, it is necessary to determine the required selectivity, capacity or reactor length necessary to achieve the assumed conversion. These parameters can be determined experimentally or much more simply, on the basis of a math-

ematical model of the reactor. For a given process, knowing its kinetics, based on the mathematical model of the reactor, it is possible to determine the reactor length necessary to achieve the assumed conversion rate, and the amount and temperature of the catalyst. One of the proposed models is one-dimensional (1D) model, which, in its complete form, is quite complex and requires knowledge of many parameters. Therefore, for various applications, some simplifications are allowed, which do not significantly affect the accuracy of the calculations. In the available literature, modelling of a reactor packed with solid foam is usually carried out using 1D model with various simplifications. One of the most commonly used simplifications is to neglect the dispersion phenomenon. However, this simplification is correct for long straight channels (e.g. like in monoliths). Therefore, the aim of the work was to check the correctness of applying this simplification in modelling of three-dimensional stochastic structure, such as a solid foam. Experimental tests were carried out to verify modelling results.

2. METHODS

The morphological characteristics of the foam used as the structural filling of the reactor were found on the basis of computer microtomography (μCT; SkyScan) combined with the iMorph software (Brun et al., 2007). On its basis, foam porosity $\varepsilon = 0.86$, specific surface area $S_v = 3143$ m^2/m^3 and hydraulic diameter $d_h = 4\varepsilon/S_v = 1.09$ mm were determined.

Measurements of heat transfer were made in an installation equipped with a system of rotameters and thermocouples enabling control and measurement of gas temperature in front of and behind the foam. In addition, the temperature on the foam surface was measured on both the inlet and outlet sides. The Joule effect was used to heat the metal foam. A more detailed description of the measuring apparatus can be found in earlier work (Sindera et al., 2022). Based on the measurements carried out, the equation for the Nusselt number was determined.

$$Nu = 0.206 Re^{0.794} Pr^{\frac{1}{3}} \tag{1}$$

The hydraulic diameter of the foam was taken as the characteristic linear dimension. The Reynolds number was determined with the formula:

$$Re = \frac{v d_h \varrho}{\varepsilon \mu} \tag{2}$$

The Sherwood number was determined using the Chilton-Colburn analogy and Equation (1).

A layer of Al_2O_3 washcoat was applied to the surface of the foam by electrodeposition. Then the washcoat layer was covered with catalytically active palladium in the amount of 0.45% by weight of the washcoat.

Methane oxidation measurements were carried out in an installation equipped with a gas flow control system and a temperature control system in the reactor. Air containing 4000 ppm of methane was used for the tests. The process was carried out at the reactor inlet temperatures of 250, 300, 350 and 400 degrees Celsius and two gas flow rates of 200 and 500 ml/min under normal conditions ($T = 273.15$ K, $p = 101325$ Pa). The diameter of the reactor was 28 mm and the height of the catalytic bed was 45 mm.

Matlab software was used for mathematical modelling, enabling a numerical solution to the problem of boundary values presented in the poster of the system of differential equations. Calculations were performed using one-dimensional reactor model. Three cases were considered in this model:
A) isothermal process,
   this simplification was chosen because purified air contains a very small amount of methane (0.4 vol%). According to (Kołodziej and Łojewska, 2016) such a simplification is acceptable under certain conditions;
B) a process that takes into account the heat of reaction (Gancarczyk et al., 2018);
C) same as process B with additional consideration of longitudinal dispersion.

The longitudinal dispersion coefficient was determined according to Equation (3) (Saber et al., 2012)

$$D_{ax} = 2.4 \cdot 10^{-3} v \tag{3}$$

The Arrhenius equation for the tested catalyst was determined as:

$$k_r = 49.16 \cdot \exp\left(\frac{69.4 \cdot 10^3}{RT}\right) \tag{4}$$

In the calculations, the value of the effectiveness factor, η, was assumed to be equal to 1, because the Thiele modulus in the analysed case was less than 0.5.

The physical properties of pure air were used in the calculations, as the maximum concentration of methane at the reactor inlet was 4000 ppm (0.4 vol%).

Viscosity (Pa·s) was calculated according to (Green and Perry, 2008):

$$\mu = \frac{1.425 \cdot 10^{-6} T^{0.5039}}{1 + \frac{108.3}{T}} \tag{5}$$

Air density (kg/m^3) was calculated from the ideal gas equation of state:

$$\varrho = \frac{p}{287T} \tag{6}$$

The enthalpy of methane combustion reaction at the temperature of 250 °C is −802.4 kJ/mol, and at the temperature of 550 °C, −799.4 kJ/mol, because the change in the tested temperature range is small, a constant average value of $\Delta H_r = -800.9$ kJ/mol was assumed in the calculations. Enthalpy calculations were made on the basis of enthalpies of pure reagents (Barin, 1995).

3. RESULTS

Figure 2 in the poster shows a comparison of the analysed models and the results of the experiments. Figure 2 shows that for each of the tested gas flow rates, models B and C predict the degree of conversion well from the measurement data. The isothermal model (A) differs significantly from other models and experimental data.

Figure 3 shows the degree of methane conversion along the catalyst bed according to model C and compares the obtained results with experimental data at the reactor outlet. Data is shown for each temperature and flow rate tested. The mathematical model reflects the experimental data well, the largest differences are visible for the temperature of 350 °C.

Figure 4 shows a comparison of the degree of methane conversion at different temperatures with experimental data. Model C was used in the calculations. A good fit to the experimental data was obtained. The greatest difference is observed for the temperature of 350 °C.

Figure 5 presents a summary of numerical calculations for each of the tested models. The figure shows that the most important thing in the tested process is to take into account the reaction enthalpy, while the longitudinal dispersion in the tested flow range has no significant effect on the course of the process.

4. CONCLUSIONS

1. Models B and C give similar results in line with experiments, it follows on from that the heat balance cannot be omitted in modelling.
2. In the tested conditions, the omission of longitudinal dispersion does not significantly affect the modelling results.
3. As the temperature increases, the degree of methane conversion along the reactor increases. $\sim 90\%$ conversion for an inlet temperature of $400\,°C$ is achieved with a bed length of ~ 2 cm.
4. Models B and C agree with the experimental data with satisfactory accuracy.

ACKNOWLEDGEMENTS

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Introduction

Interest in conducting a chemical process on catalysts deposited on various types of structures has increased in recent years. One of them is open-cell solid foam. Such support is characterized by a low density of approx. 3% compared to bulk material and high thermal conductivity compared to classic ceramic catalyst carriers. These properties favorably affect achieving fast catalyst light-off. In addition, solid foams are characterized by much better mass transport and reactant mixing than in a classic cordierite monolith.

As the catalyst support was used the Fecralloy foam with a pore density of 16 PPC (pores per centimeter). Washcoat was prepared by the electrochemical deposition method. This method enables the direct formation of Al_2O_3 on different metal surfaces. The catalyst was prepared by incipient wetness impregnation technique using a palladium nitrate solution. The impregnated foam disks were subsequently calcined in stationary air to obtain palladium nanoparticles on the surface.

Methane oxidation tests were carried out in a tubular reactor with a precise temperature control system. The catalytic packing consisted of stacked foam discs. The experiments were carried out for the following conditions: GHSV in the range of 430 and 1083 hr^{-1}; bed temperature in the range of 250 – 400 °C; the concentration of methane in the air was 4000 ppm.
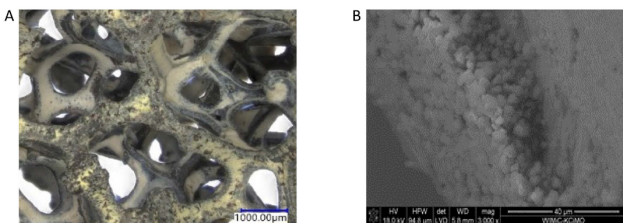

Fig. 1. Solid foam with a palladium catalyst, picture from a) Keyence microscope, b) SEM

Mathematical model

The reactor model combines mass and heat balances with kinetic parameters of a chemical reaction and packaging transport parameters. In the most general case (one-dimensional model), the mathematical model of the reactor consists of a differential mass balance, which for the key reactant A has the form:

$$\left(\varepsilon \frac{\partial C_A}{\partial t} \right) + w \frac{\partial C_A}{\partial x} - \left(D_{ax} \frac{\partial^2 C_A}{\partial x^2} \right) + S_v k_c (C_A - C_{As}) = 0$$

and heat balance:

$$\left(\varepsilon \rho c_p \frac{\partial T}{\partial t} \right) + w \rho c_p \frac{\partial T}{\partial x} - \left(\lambda_{ax} \frac{\partial^2 T}{\partial x^2} \right) + h S_v (T - T_s) + \left(\frac{O}{A_c} k_H (T - T_w) \right) = 0$$

$$k_c (C_A - C_{As}) = \eta(-r_A) = \eta k_r C_{As}$$

$$h(T_s - T) = -\Delta H_r \eta(-r_A)$$

where: C_A – concentration, t – time, w – velocity, D_{ax} – longitudinal dispersion coefficient, S_v – specific surface area, k_c – mass transfer coefficient, C_{As} – concentration on the catalyst surface, ε – porosity, ρ – density, c_p – specific heat, λ_{ax} – axial heat transfer coefficient, h – heat transfer coefficient, T_s – catalyst surface temperature, O – reactor perimeter, A_c – reactor cross-sectional area, k_H – overall heat transfer coefficient, T_w – reactor wall temperature, ΔH_r – reaction enthalpy, r_A – reaction rate, k_r – reaction rate constant, η – effectiveness factor defined by Thiele modulus.

Simplifications

Model A

$$w \frac{\partial C_A}{\partial x} + S_v k_c (C_A - C_{As}) = 0$$

Model B

$$w \frac{\partial C_A}{\partial x} + S_v k_c (C_A - C_{As}) = 0$$

$$w \rho c_p \frac{\partial T}{\partial x} + h S_v (T - T_s) + \left(\frac{O}{A_c} k_H (T - T_w) \right) = 0$$

Model C

$$w \frac{\partial C_A}{\partial x} - \left(D_{ax} \frac{\partial^2 C_A}{\partial x^2} \right) + S_v k_c (C_A - C_{As}) = 0$$

$$w \rho c_p \frac{\partial T}{\partial x} - \left(\lambda_{ax} \frac{\partial^2 T}{\partial x^2} \right) + h S_v (T - T_s) + \left(\frac{O}{A_c} k_H (T - T_w) \right) = 0$$
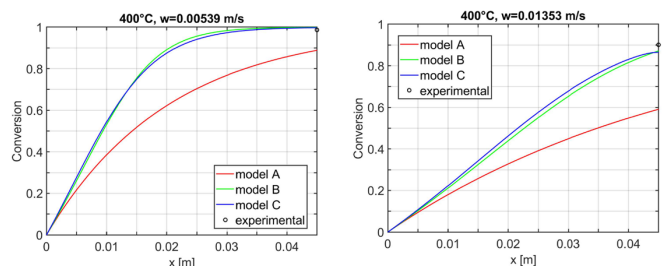
Results

Fig. 2. Comparison of mathematical models with experimental data for GHSV 430 and 1083 hr^{-1}.
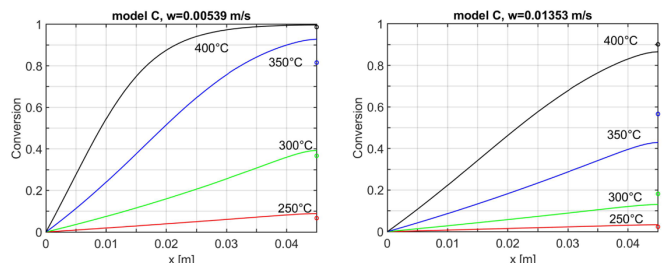

Fig. 3. Methane conversion along the catalytic bed for different temperatures according to model C.
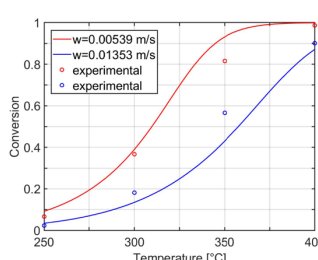

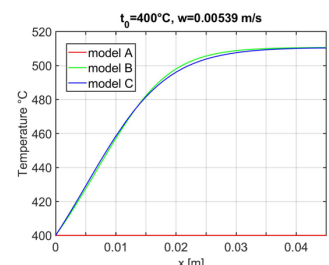Fig. 4. Comparison of experimental values with prediction using the C model.

Fig. 5. Changes in the temperature of the catalytic bed along its length.

Conclusion

The simplifications used in the modeling of a chemical reactor with a catalytic bed made of solid foam make it possible to estimate the dimensions of the reactor with good accuracy in relation to the assumed input parameters of the purified gas. The most important parameter influencing the calculations is the kinetics of the process.